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THE USE OF APPARENT MOLECULAR WEIGHT DISTRIBUTION TO EVALUATE THE TRANSFORMATION OF NATURAL ORGANIC MATTER DURING OZONATION AND BIOLOGICAL TREATMENT

By

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ABSTRACT

THE USE OF APPARENT MOLECULAR WEIGHT DISTRIBUTION TO EVALUATE THE TRANSFORMATION OF NATURAL ORGANIC MATTER DURING OZONATION AND BIOLOGICAL TREATMENT

By

Julie A. Mellema

The effects of combined ozonation and fluidized bed treatment (FBT) on the apparent molecular weight distribution of natural organic matter (NOM) in Huron River water were investigated using bench-scale and small pilot-scale systems. The total organic carbon (TOC) level in all of the apparent molecular weight fractions (determined by ultrafiltration) was reduced by FBT. Experiments conducted using ozonation/FBT indicated that at low ozone doses (0.5 and 1.0 mg/mg C), ozone simultaneously oxidized high and low apparent molecular weight compounds. However, at ozone doses greater than 1.0 mg/mg C, ozone was used more efficiently. The ozonation/FBT system was then modified to a FBT/ozonation system to allow the FBR to remove the biodegradable compounds first, and then ozonate compounds that were not biodegradable.

Experiments were conducted to determine the relationship between the low molecular weight fraction (<500 daltons), and biodegradability. A linear relationship existed between biodegradable organic carbon and TOC, indicating that water treatment utilities can use ultrafiltration to determine biodegradation potential, thus eliminating the need for time-consuming biodegradability experiments.

To anyone attempting to author a master's degree thesis:

"When nothing seems to help, I go look at a stone cutter hammering away at his rock
perhaps a hundred times without as much as a crack showing in it.
Yet at the hundred and first blow it will split in two,
and I know that it was not that blow that did it
– but all that had gone before."

-Jacob Riis

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LIST OF ABBREVIATIONS

AWWA	American Water Works Association
AOC	Assimilable Organic Carbon
BDOC	Biodegradable Organic Carbon
D/DBP	Disinfectants/Disinfection By-Products
DBP	Disinfectant By-Products
DOC	Dissolved Organic Carbon
FBR	Fluidized Bed Reactor
FBT	Fluidized Bed Treatment
GAC	Granular Activated Carbon
GPC	Gel Permeation Chromatography
HAA	Haloacetic Acid
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MRDL	Maximum Residual Disinfectant Level
MRDLG	Maximum Residual Disinfectant Level Goal
MW500	Molecular Weight Compounds <500 Daltons
NOM	Natural Organic Matter
SDWA	Safe Drinking Water Act
SWTR	Surface Water Treatment Rule
TCR	Total Coliform Rule
THM	Trihalomethanes

THMFP	Trihalomethane Formation Potential
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency

CHAPTER 1

INTRODUCTION

1.1 Research Objectives

The ultimate goal of this study was to determine the effects of ozonation and fluidized bed treatment (FBT) processes on the apparent molecular weight distribution of natural organic matter (NOM). Particular objectives of this study were:

- To develop a protocol for determining apparent molecular weight distribution.
- To determine the effect of biological treatment on the apparent molecular weight distribution of NOM.
- To determine the effect of ozone dose on the apparent molecular weight distribution of NOM during ozonation and FBT.
- To determine the effect of combined ozonation and biological treatment on the apparent molecular weight distribution of NOM.
- To develop optimization strategies for the ozonation/FBR treatment process by identifying the interrelationships between the apparent molecular weight distribution of fractionated organic matter and its treatability.
- To establish the relationship between low apparent molecular weight compounds (<500 daltons) and biodegradability of NOM.

1.2 Background

1.2.1 The Significance of Natural Organic Matter. Surface waters contain natural organic matter (NOM) formed by natural processes such as the microbial decay of vegetation. NOM constitutes a major portion of the total organic carbon (TOC) present in most waters [1]. NOM is made up of amino acids, carboxylic acids, proteins, carbohydrates, and aquatic humic substances. Approximately thirty to fifty percent of NOM present in surface waters consists of aquatic humic substances [2], which are colored, polyelectrolytic organic acids that are defined by their sorption onto XAD or weak-base ion exchange resins [3]. Major functional groups of humic substances include carboxylic acids, phenolic hydroxyl, carbonyl and hydroxyl groups. Aquatic humic substances are the most important component in NOM due to their abundance and their reactivity.

Aquatic humic substances consist of two fractions, humic and fulvic acids; fulvic acids constitute the majority of all aquatic humic substances [3]. The molecular weight of aquatic fulvic and humic acids ranges from 500 to 10,000 daltons. Humic acids are generally higher molecular weight compounds (>2000 daltons), than the fulvic acids (<2000 daltons). Therefore, most aquatic humic substances are dissolved rather than colloidal.

The presence of aquatic humic substances in surface waters poses several problems for water treatment utilities. These include color, odor, taste, increased chemical disinfectant demand, and the formation of disinfectant by-products (DBPs) such as trihalomethanes (THMs) [4]. Aquatic humic substances play a large role in water treatment due to the generation of THMs and other organo-chlorine compounds during

chlorination [5]. Chlorine, which is the most commonly used water disinfectant in the U.S., reacts with the aquatic humic substances to form organic and inorganic DBPs. It has been found that humic substances are the predominant precursors that react with chlorine and bromine to produce THMs and other halogenated DBPs [1]. It has also been found that THMs are the leading DBPs found in treated water, followed by haloacetic acids (HAAs) [6].

1.2.2 Regulatory Background. Disinfection by-products such as THMs and haloacetic acids (HAAs) are potentially carcinogenic and have recently become more stringently regulated by the U.S. Environmental Protection Agency (USEPA) under the Safe Drinking Water Act (SDWA) [1,7]. The goal of the SDWA is to reduce the chronic risk of DBPs in drinking water supplies and to provide microbiologically stable drinking water. Therefore, a Disinfectants/Disinfection By-Products (D/DBP) Rule was proposed to set limits on residual concentrations of DBPs and disinfectants. As a result of the D/DBP Rule, NOM has recently become more of a concern in the water treatment industry.

In 1994, the USEPA proposed a Stage 1 D/DBP Rule which established Maximum Contaminant Level Goals (MCLG), Maximum Contaminant Levels (MCL), Maximum Residual Disinfectant Level Goals (MRDLG), and Maximum Residual Disinfectant Levels (MRDL) for several DBPs and disinfectants (Table 1.1). MCLs are enforceable limits on contaminants, and MRDLs are enforceable limits on residual disinfectants. Although both MCLGs and MRDLGs are goals that cannot be enforced, water utilities are encouraged to meet these limits. Under the Stage 1 D/DBP Rule, the MCL for total THMs was lowered from 0.10 mg/L to 0.08 mg/L, and an MCL of 0.06

mg/L for the sum of five haloacetic acids (HAA5) was added (40 CFR Parts 141 and 142) [7]. The THMs regulated by the D/DBP rule include chloroform, bromodichloromethane, chlorodibromomethane, and bromoform, and the HAAs regulated by the D/DBP rule include mono-, di-, and trichloroacetic acids and mono- and dibromoacetic acids. MCLs were also implemented for bromate and chlorite, and MRDLs were implemented for chlorine, chloramine, and chlorine dioxide [8] (Table 1.1).

In 1997, amendments were made to the Stage 1 D/DBP Rule based on a reassessment of the 1994 proposal. According to the Information Collection Rule, modifications can be made when new available information is presented. Therefore, several changes to the Stage 1 D/DBP Rule were made when new toxicological information for several DBPs was reviewed. The 1997 amendment also required the USEPA to promulgate a Stage 1 D/DBP Rule by November of 1998, and a Stage 2 D/DBP Rule by May 2002 (40 CFR Parts 141 and 142). The Stage 2 D/DBP Rule proposed an MCL of 0.04 mg/L for total THMs and an MCL of 0.03 mg/L for HAA5 [7]. However, Stage 2 regulations are tentative and may be modified based on the Information Collection Rule, which is presently in effect. Displayed in Table 1.1 are the regulations under the Stage 1 D/DBP Rule that were proposed in 1994 and 1997.

Table 1.1. USEPA Regulations according to the Stage 1 D/DBP Rule.

MCLs	1994	1997
Total THMs	0.08 mg/L	0.08 mg/L
HAA5[1]	0.06 mg/L	
Bromate	0.01 mg/L	0.01 mg/L
Chlorite	1.0 mg/L	1.0 mg/L
MCLGs	**1994**	**1997**
Chloroform	0 mg/L	0.3 mg/L*
Bromodichloromethane	0 mg/L	
Bromoform	0 mg/L	
Bromate	0 mg/L	0 mg/L
Dichloroacetic acid	0 mg/L	0 mg/L
Dibromochloromethane	0.06 mg/L	
Trichloroacetic acid	0.3 mg/L	
Chloral Hydrate	0.04 mg/L	
Chlorite	0.08 mg/L	0.8 mg/L*
MRDLs	**1994**	**1997**
Chlorine and Chloramine	4.0 mg/L	
Chlorine Dioxide	0.8 mg/L	0.8 mg/L
MRDLGs	**1994**	**1997**
Chlorine and Chloramine	4.0 mg/L	
Chlorine Dioxide	0.3 mg/L	0.8 mg/L*

[1] Only five of the nine Haloacetic Acids are regulated.
* Changed from the 1994 proposed value.

1.2.3 Treatment Methods. In the past, water treatment facilities have used chemical coagulation, activated carbon adsorption, and oxidative techniques to meet the USEPA regulations. The most widely used process in the water treatment industry is chemical coagulation. This conventional treatment method requires chemical addition, rapid mixing, and flocculation. Chemical coagulation removes suspended materials by colloidal destabilization, and dissolved NOM by precipitation or coprecipitation. Chemical coagulation is sometimes used as a pretreatment to granular activated carbon (GAC) adsorption or filtration, which is commonly used in the United States for the removal of taste and odor from surface waters. Chemical coagulation is commonly used

to reduce the loading on subsequent treatment processes, to increase the adsorptive capacity in the GAC column, and to remove larger materials that could clog the GAC column.

However, in order to remove adequate concentrations of NOM to meet the new DBP regulations, water treatment facilities need to consider alternative treatment technologies. Many treatment strategies have been investigated to improve the quality of drinking water in order to control the amount of DBPs. The USEPA has suggested that the best available technology to meet the MCLs for total THMs and HAAs is enhanced coagulation or GAC with chlorine for primary and residual disinfection (40 CFR Parts 141 and 142, p. 15676). This is because it does not require major capital investments. The D/DBP Rule defines enhanced coagulation as the addition of excess coagulant to the conventional treatment process for improved removal of DBP precursors [9]. Additional changes in the conventional treatment methods can be made, in which the point of chlorination is moved downstream in the treatment process, the chlorine dose is decreased, or chloramines, rather than free chlorine, are applied as a primary and secondary disinfectant [1]. These changes have been considered primarily in small treatment facilities that cannot afford the extensive capital costs involved in converting to a completely different treatment system. However, there are several disadvantages to enhanced coagulation including 1) increased sludge production from the increased coagulant dose, 2) increased chemical costs for coagulation and final pH adjustment, 3) increased chemical storage and feed facilities, and 4) optimum turbidity removal may not be achieved. Also, there was major concern with the microbial quality of the treated water from these systems. Even when the DBP regulations are met by enhanced

coagulation, the water still may not pass the Surface Water Treatment Rule (SWTR) or the Total Coliform Rule (TCR), which regulates *Giardia* and other viruses in the drinking water [8]. Rarely does an existing water treatment facility provide the required contact time for inactivation of such viruses [9]. Therefore, alternative treatment technologies need to be developed.

Another treatment alternative for the control of DBP formation is ozonation. Ozone has been a common method of water treatment in European countries since the early 1900's. It is known to be effective for disinfection and the oxidation of color, odor, hydrogen sulfide, iron and manganese [10]. Studies have shown that ozone is a better coagulant than chlorine [11], and water treated using ozonation is less mutagenic than that treated using chlorine or chlorine dioxide [12]. Finally, the free radical decomposition products of ozone are better oxidizing agents than either chlorine or ozone [13]. Ozone is also useful for the oxidization of humic substances into more biodegradable compounds, the reduction of light absorbance properties, such as ultraviolet (UV) absorbance and turbidity, the decrease of TOC, the increase in lower molecular weight compounds, and the decrease in THM formation potential (THMFP) [13-16].

Ozone has two major limitations. First, ozone has a short half-life at typical drinking water pH (~8) and, therefore, does not provide residual disinfection potential in distribution systems. Ozone is, however, more effective than chlorine for the removal of *Giardia* and other viruses [13]. Second, ozone changes the character of NOM producing low molecular weight oxygenated byproducts that are more biodegradable than their precursors. Thus, it is necessary to provide additional treatment downstream from

ozonation in order to remove this material, and thereby, prevent bacterial regrowth in the distribution system [13].

Due to the ability of ozone to reduce humic substances to more biodegradable forms, researchers have found that using ozonation in conjunction with biological treatment produces exceptional quality water. [17-18]. Therefore, ozone can be used to oxidize humic substances and other NOMs to form biodegradable products, which can be subsequently removed by biological treatment. Ozonation followed by biological treatment has been implemented in Western Europe in which ozonation precedes GAC filtration. This treatment method is referred to as biological activated carbon [13]. Due to changes in the NOM by ozone, the biological activity is increased in biofiltration downstream in the treatment train [14,19]. Malley et al. also found that ozone enhances the filter performance in conventional slow sand filtration processes for compliance with the D/DBP Rule [20]. The byproducts formed by ozone oxidation are more biodegradable than byproducts formed during chlorination and therefore allow removal of more NOM and THM precursors in the biological treatment.

Until recently, the use of ozone to treat drinking water was only applied in Europe [13]. The United States has been slow to accept ozonation for the treatment of surface water due to cost, compliant water quality by alternate methods, and tolerance of chlorine taste by the consumers [10]. There have also been problems with equipment failures caused by incorrect design and specification of ozone systems [21]. In the past, conventional U.S. treatment methods have met drinking water regulations, and there was not a dire need for alternate treatment technologies until the D/DBP Rule was introduced. The D/DBP Rule will force the U.S. to consider alternative treatment methods to meet the

new stringent regulations. Due to the lowered MCL for THMs, it will be necessary for a number of treatment facilities to eliminate the use of free chlorine and severe restrictions will be set for the use of chlorine dioxide. An improved disinfection scheme could include ozone as the primary disinfectant and chloramines as the residual disinfectant [10]. However, additional research needs to be conducted to determine the effects of ozone byproducts that are formed during ozonation.

1.2.4 Apparent Molecular Weight Distribution – Discussion of Methods. Due to the stringent regulations proposed in the D/DBP Rule, properties of natural aquatic substances need to be investigated to achieve optimal removal from drinking water supplies. Molecular weight is one property that has a significant impact on the removal of natural aquatic substances. Researchers have observed that the THM yield or reactivity of natural aquatic substances also varies with molecular weight [5]. The majority of THMs formed are derived from organics with molecular weight less than 10,000 daltons [22]. Studies have shown that different treatment techniques are more effective for the removal of different molecular weight fractions [23]. The applicability of the treatment process to the water source depends on the apparent molecular weight distribution. The lower molecular weight compounds tend to be hydrophilic and are not likely to be removed by coagulation or adsorption. The adsorptive capacity for the lower molecular weight fractions is, however, greater than that of the higher molecular weight compounds. This may be due to exclusion of large molecules from the smaller pores of the activated carbon. Low molecular weight compounds are more effectively removed by oxidative processes, and medium and higher molecular weight compounds are more effectively removed by GAC and coagulation, respectively [23-24]. Appropriate

treatment processes are generally selected to specifically remove certain molecular weight fractions of the aquatic humic substances that form DBPs during disinfection.

Since humic substances consist of a complex mixture of polyprotic anions of varying molecular weight, functionality, and hydrophobicity, there is no direct method of measurement of NOM in source waters [23]. Therefore, the characterization of NOM is commonly based on apparent molecular weight distribution, which determines the size distribution of dissolved organic matter present in the source water and in samples taken at different stages in treatment systems. Therefore, apparent molecular weight distribution, expressed in terms of total organic carbon (TOC), UV absorbance, and trihalomethane formation potential (THMFP), can be used to assess the applicability of treatment strategies for specified source waters and to monitor the performance of given treatment processes [23]. The size of the dissolved organics will be referred to in this paper as "apparent molecular weight" rather than "apparent molecular size", since analytical methods are calibrated by compounds of known molecular weight, not size. Several methods have been used to determine the apparent molecular weight distribution of organic matter in water supplies. The two most commonly used methods to determine apparent molecular weight distribution are gel permeation chromatography (GPC) and membrane ultrafiltration [5].

1.2.4.1 Gel Permeation Chromatography (GPC). GPC is a size exclusion chromatography which involves a specified type of gel that is characterized by the molecular weight range over which molecules can be fractionated. The gel is calibrated by the use of proteins and other biochemicals with known molecular weights. It is somewhat inaccurate to use calibration curves obtained from proteins and biochemicals

due to differences in charge, shape, and hydration in the humic material [4]. Overestimation of molecular weight may occur when some compounds pass through the column at a faster rate than the calibration standards, or underestimation of molecular weight may occur when compounds are slowed by adsorption or electrostatic interaction with column packing.

Problems may also occur in the GPC method when evaluating the molecular weight distribution of NOM in surface waters. The concentrations of natural aquatic substances may not be high enough to maintain measurable levels of organic matter after the sample has been diluted by the eluent. Also, the interaction between solute molecules in the sample may cause molecular aggregates to form and result in a false representation of the high molecular weight compounds. The interaction of organic matter in the water supply may be influenced by the concentration in the water, the presence of polyvalent cations, the pH, and the ionic strength. Other problems that arise when using GPC depend on the composition of the eluent. The eluent has a major impact on the gel, the humic substances in the water, and the interactions between the gel and the humic substances. The pH and the ionic strength of the eluent are significant factors affecting the solubility of the humic substances, and the ionization of function groups that may reduce the hydrogen bonding with the resin [4].

1.2.4.2 Ultrafiltration. Another method of molecular weight distribution is membrane ultrafiltration. The concentration of organic matter having a specific molecular size is quantified by the measurement of total organic carbon or UV absorbance. The sample is passed through the membrane by means of convective flow, and the membrane selectively rejects solutes in the water samples. Each membrane has a

specified cutoff weight in which the larger solute molecules are retained as part of the retentate, and the smaller solute molecules are passed through the membrane as part of the permeate. The molecules migrate through the membrane both by advective flow and molecular diffusion. The solute flux is greatly dependent on the area of the membrane, the concentration gradient, and molecular diffusion [4].

The size and shape of the molecules determine the rate at which diffusivity will occur. Small molecules will diffuse much faster than the larger ones, and spherical molecules will diffuse much faster than linear ones of a similar molecular weight [4]. Problems may arise in the fractionation of organic matter in the water samples due to misleading results based solely on the molecular weight with no consideration of the molecular shape. The molecular shape and the steric properties have a major influence on the flux through the membrane as evidenced by molecules with similar molecular weights that tend to exhibit very different retention behavior. However, studies have been conducted to verify that the molecular weight cutoff of a membrane consistently corresponds to the actual molecular weight of the compound [4].

The concentration gradient across the ultrafiltration membrane also has a major effect on the flux of the water sample through the ultrafiltration membrane. Studies have shown that the higher the concentration of NOM in the sample, the greater the retention of the higher molecular weight compounds, and the lower the retention of the lower molecular weight compounds [4]. The flux of the sample through the membrane increases as the concentration differences in the two fluid regions on either side of the membrane increases. Concentration polarization occurs when the larger molecules adsorb to the sides of the membrane pores and form a gel layer, which restricts the flow

through the membrane. Possible inaccuracies in the results may occur as the gel layer blocks the larger molecules and only allows the very small molecules to pass through the membrane. The most common ways of reducing concentration polarization are to rapidly stir the sample in the ultrafiltration cell, and to use a pressurized vessel to maintain a constant level of sample in the ultrafiltration cell. Also, proper care of the membranes greatly reduces the effects of concentration polarization on the sample.

Another problem with fractionation by ultrafiltration occurs when membrane rejection is neglected. Membrane rejection is a function of solute concentration at the surface of the membrane that causes compounds smaller than the apparent molecular weight cutoff of the membrane to remain in the retentate. Therefore, substantial underestimation of the low molecular weight compounds may result when rejection properties of the ultrafiltration membrane are not considered. A study conducted by Logan and Jiang in 1990 [22], introduced a simple method to account for membrane rejection and to correct the size distribution of NOM during batch ultrafiltration. The method uses rejection coefficients that are experimentally determined by monitoring the instantaneous change in the permeate concentration for the specified sample and membrane. The rejection coefficient accounts for the rejected molecular weight fractions below the cutoff and produces more precise estimates of molecular weight [14, 22, 23]. However, when a consistent ultrafiltration procedure is maintained, the apparent molecular weight results will define relative differences in samples throughout various treatment processes, and rejection coefficients are not necessary. Therefore, when continuous ultrafiltration is used, the results will represent relative changes in samples, but not precise estimates of molecular weight [22-23].

1.2.4.3 Conclusions. The US Geological Survey commonly uses GPC and ultrafiltration to determine the apparent molecular weight distribution of the overall dissolved organic carbon or of isolated humic substances [4]. Membrane ultrafiltration and GPC are both inexpensive analytical techniques that require only moderate levels of analyst expertise. Both methods of molecular weight distribution would give an adequate representation of organic matter in raw water sources as well as the removal of organic matter during water treatment [4]. Amy et al. showed that although GPC may display higher molecular weight estimates than ultrafiltration, both methods exhibited the same general trends in the apparent molecular weight distribution [15]. However, one advantage of ultrafiltration over GPC is the ability to process large sample volumes that can be recovered and used for further characterization [22]. Also, ultrafiltration is the only method available to characterize compounds in the lowest apparent molecular weight fraction (<500 daltons) [4]. Therefore, ultrafiltration was the chosen method of analysis for molecular weight distribution in this project.

1.3 Literature Review

1.3.1 Related Research on Ozone/Biological Treatment. The American Water Works Association (AWWA) funded a research project in 1992, to investigate the effects of ozone/biological treatment on the removal of DBPs and the production of biologically stable drinking water [10]. Two processes were evaluated to determine the impact of ozonation on the NOM in the water. The first process consisted of ozonation followed by anthracite/sand dual media filters followed by GAC or GAC/sand dual media filters. The second process was identical to the first process, but without the ozonation stage.

Results from this study showed that ozonation significantly increased biodegradability and decreased THM formation potential in the water. Results also showed that ozone increased assimilable organic carbon (AOC) and aldehyde levels in the water [10]. Other problems related to the use of ozone included inconsistent reduction in DBP concentrations, an increase in the formation of brominated compounds when bromide ion is present, and the formation of ozone byproducts such as aldehydes, keytones, and carboxylic acids [10]. However, when ozonation was followed by biological treatment, the aldehyde levels were reduced by biological activity. While the AOC levels were also reduced, their concentrations did not return to the original pre-ozone level. The biological process also reduced THM formation potential. The results from this AWWA project indicated that biological filtration removes nearly all by-products created during ozonation, however, additional by-products may be formed if chlorination is used for residual disinfection [10].

Another recent study was conducted to determine the effect of ozonation and biological treatment on surface waters [19]. Experiments were conducted using water from Lake Austin in Texas. The water characteristics in Lake Austin were comparable to the Huron River water used in this project. Lake Austin samples were ozonated, and then recirculated through columns containing an acclimated biofilm. The TOC concentration was monitored to determine the amount of biodegradation at the different ozone doses. It was determined that the rate and extent of biodegradation, and the TOC removal increased with ozone dose. Also, it was found that chlorine residuals were higher in ozonated and biodegraded water, but the formation of DBPs was lower. These results indicate that the biological treatment removed some DBP precursors from the samples.

Therefore, ozonation followed by biofiltration appeared to be an effective treatment method for removing DBP precursors, increasing chlorine residuals, reducing chlorine dose, and decreasing biological regrowth [19].

1.3.2 Related Research on the use of Apparent Molecular Weight Distribution. Amy et al. [15] found that ozonation affects the apparent molecular weight distribution of humic substances in water sources. Experiments were conducted with the use of both GPC and ultrafiltration to determine the apparent molecular weight distributions of untreated and ozonated water samples. Each sample was characterized according to DOC, UV absorbance, and THMFP. Results showed that the ozone decreased the THMFP and the ratio of UV absorbance to DOC, or specific absorbance, in all of the waters investigated. These results indicated that ozone removed the UV light absorbing molecules, but did not oxidize the organic carbon into carbon dioxide and water. Therefore, ozonation by-products were less reactive with chlorine, as indicated by the lower THM reactivity, which is the ratio of THMFP to DOC.

Results also showed that partial oxidation was achieved by ozone in which the larger apparent molecular weight fractions were broken down into smaller apparent molecular weight oxidation byproducts. Ozone significantly decreased the high molecular weight fractions (>20,000 daltons), which produced a corresponding increase in the low molecular weight fractions (<500 daltons). Although there was no overall DOC removal in half of the waters investigated, ozone still caused a major change in the apparent molecular weight distribution in all samples, and there was a reduction in the THMFP in all samples.

Experiments have also been conducted to determine the effect of biological treatment on the apparent molecular weight distribution of NOM [14]. Results have indicated a possible correlation between biodegradable organic carbon and the molecular weight distribution of the NOM in the water sample. It was expected that lower molecular weight compounds would be more biodegradable than higher molecular weight compounds. Compounds with lower molecular weight generally exhibit lower mass transfer resistance and greater accessibility for enzymatic attack [14]. Also, enzyme-catalyzed hydrolysis, a very slow process, may be required to break down the higher molecular weight compounds into lower molecular weight compounds [14].

Goel et al. [14] found the UV-to-TOC ratio to be an indicator of relative biodegradability. This ratio represents the amount of unsaturated chemical bonds in the organic compounds since UV-light is predominantly absorbed by unsaturated C-C bonds. It was shown that the higher the UV-to-TOC ratio, less TOC was removed by biodegradation. Results of some studies even suggest that the UV-to-TOC ratio is a better predictor for biodegradability than apparent molecular weight distribution [14]. However, drinking water facilities have used both apparent molecular weight distribution and UV-to-TOC ratios as easy, affordable methods for evaluating biodegradation potential of source waters [14].

1.4 Description of Study

1.4.1 Experimental Treatment Method. This study utilized a proposed ozonation/fluidized bed treatment (FBT) process for the control of DBP precursors. The use of ozonation in combination with FBT is an innovative alternative to the conventional

ozonation/biofiltration process. FBT has been used for the past ten years to treat process waters and groundwaters that contain volatile organic compounds and chlorinated solvents [25]. FBT uses a fluidized bed reactor (FBR) which prevents clogging, a common problem in biofiltration. Therefore, ozonation/FBT systems may not require pretreatment as is necessary with ozonation/biofiltration systems. The FBR also provides a larger specific surface area than biofiltration, thereby increasing the concentration of attached biomass in the reactor. Hence, the removal efficiency in the FBT is expected to be higher than in the conventional biofiltration systems [26]. Ozonation/FBT also offers the option of operating in cyclic mode, whereas most ozonation/biofiltration processes are single-pass processes. Cyclic ozonation/FBT consists of alternately passing water through the ozonation and FBT processes to improve the treatment efficiency and decrease ozone consumption by only utilizing ozone for compounds that are not biodegradable [26].

1.4.2 NOM Characterization. Membrane ultrafiltration, in terms of TOC, was used in this study to define the apparent molecular weight distribution of NOM evaluated at different stages in the combined ozonation/FBT treatment process. Apparent molecular weight distribution can be used to display trends in NOM at different stages of the treatment processes. Therefore, it can be used to monitor the treatment performance, and identify interrelationships between the organic matter in water and its treatability. Although research of aquatic humic substances has indicated that ultrafiltration may not be a well suited method for obtaining precise absolute values of apparent molecular weight [2,4], it is a practical method for monitoring the transformation of organic matter during water treatment processes [15]. For comparative purposes, it is essential that the

same ultrafiltration experimental conditions are maintained for each sample. The ultrafiltration experimental setup used for each phase will be described in the subsequent chapters.

Apparent molecular weight distribution was also used in this project for the optimization of the ozonation/FBT process. However, the principal goal of the apparent molecular weight distribution study was not to directly optimize the treatment processes for THM removal, but rather to monitor the process performance according to NOM removal. The bench-scale and small pilot-scale experimental systems were used to investigate the removal of NOM by ozonation, FBT, and combined treatment processes.

1.4.3 Research Approach. This study was divided into three different phases. The experimental systems that were used for each of these phases are presented in Chapter 2.

Phase I focused on the development of an apparent molecular weight distribution protocol for the evaluation of NOM in water samples. Several factors were taken into consideration for the development of the optimal ultrafiltration procedure. These factors included sample volume, sample concentration, operating mode (batch or continuous), and time. When determining the sample volume to be collected, the effect of increasing volume on TOC concentrations was investigated. It was hypothesized that the TOC concentration of the permeate would increase with increasing permeate volume. Various sample volumes were processed through each ultrafiltration membrane and the TOC concentration was measured at each volume. This investigation allowed for the determination of the appropriate sample volume to be collected for analysis.

Samples with different concentrations of NOM were also compared to determine how TOC concentration was affected by increasing permeate volume. Batch mode experiments were conducted with untreated Huron River water compared to biodegraded water. It was suspected that the TOC concentration in the permeate would increase more rapidly with increasing permeate volume for samples of higher concentration due to the large concentration gradient across the membrane during batch mode experiments.

The TOC concentrations determined by both batch- and continuous-mode ultrafiltration were compared. The major difference between the two processes was that the continuous mode system employed a reservoir to maintain a constant volume within the ultrafiltration cells, and the batch mode system allowed the feed volume to decrease during ultrafiltration. An increase in permeate TOC values was expected to be more profound in the batch mode system than in the continuous mode system due to the decrease in retentate sample volume in the batch mode ultrafiltration cell as the sample passed through the ultrafiltration membrane. In order to maintain consistent experimental conditions, it was determined that three samples needed to be processed on the same day for comparative purposes. Therefore, time was another consideration taken into account during the development of the apparent molecular weight distribution protocol.

In Phase II, the effect of ozonation and biological treatment processes on the transformation of NOM was evaluated based on the apparent molecular weight distribution protocol developed in Phase I. The ozonation/FBT system was operated at an ozone dose of zero to determine the effect of FBT alone on the transformation of NOM. The apparent molecular weight distribution of untreated Huron River samples was compared to the apparent molecular weight distribution of samples after FBT. It was

expected that the concentration of lower molecular weight fractions would be reduced by FBT.

The effect of ozone on the transformation of NOM in the water samples was also investigated. Samples were taken from different stages in the ozonation/FBT system to determine the apparent molecular weight distribution of NOM before and after ozonation. Past studies have shown that ozone reacts with humic substances to form molecules with hydroxyl, carbonyl, and carboxyl functional groups, increase the polarity and hydrophilicity of the reactants, decrease adsorbability, decrease double bonds and aromaticity, and shift the molecular weight distribution toward the lower molecular weight fractions [14]. It was expected that ozonation would alter the nature of NOM by forming oxidation byproducts that were more biodegradable than their precursors. Therefore, it was expected that the removal of TOC with the ozonation/FBT processes would be greater than the FBT process alone. Apparent molecular weight distribution was used to determine the effect that ozone dose had on samples taken throughout the ozonation/FBT processes. This study evaluated the transformation of the different apparent molecular weight fractions at several ozone dosages.

Further studies in Phase II were conducted to evaluate the efficiency of ozone for the oxidation of NOM in water subject to biological treatment. The system was operated with the FBT preceding the ozonation stage of the treatment process. Apparent molecular weight distribution was used to investigate the transformation of NOM during the different treatment processes. It was hypothesized that the FBT would biodegrade the lower molecular weight fractions, and ozonation would then oxidize the organic

compounds that were not biodegradable. Therefore, it was thought that ozone would be used more efficiently in biologically treated water than in untreated water.

Finally, Phase III focused on the development of a relationship between low molecular weight compounds (<500 daltons) and the biodegradability of NOM. Several effluent samples from the ozonation/FBT system were recirculated through the biodegradability system for seven days to determine the concentration of biodegradable organic carbon (BDOC). The same ozonation/FBT effluent sample was processed through the ultrafiltration YC05 membrane with a molecular weight cutoff of 500 daltons. The concentration of low molecular weight compounds (<500 daltons) in these ultrafiltration samples was then compared to the concentration of BDOC present in the seven-day biocolumn effluent sample. It was expected that the samples with higher concentrations of low molecular weight fractions would be more biodegradable, and therefore, contain a higher concentration of BDOC. Samples were analyzed for TOC.

CHAPTER 2

PHASE I – DEVELOPING A PROTOCOL

2.1 Materials

2.1.1 Water Source. The Huron River, which flows through Ann Arbor, Michigan, was the source water tested in the experimental systems. Approximately 300 gallons of raw Huron River water were collected from the Ann Arbor Water Treatment intake each month in 15- or 20- gallon barrels. The Ann Arbor Water Treatment plant uses a treatment train that consists of lime softening, floccculation/sedimentation, ozonation, granular activated carbon (GAC) filtration, and chloramination. Therefore, results obtained from the ozonation/FBT system can be compared to those obtained from the Ann Arbor Treatment Plant. The Huron River water contains high concentrations of TOC, turbidity, and suspended solids (Table 2.1). Due to these high concentrations in the surface water, the removal of TOC and THM precursors was expected to be more pronounced in the ozonation/FBT system. Also, the turbid nature of the raw Huron River water tests the ability of the ozonation/FBT system to sustain high loadings of suspended solids and turbidity without pretreatment.

Table 2.1. Typical Huron River water quality characteristics.

Parameter	Raw Water Measurement
TOC, mg/L	5.4 – 8.3
pH	7.6 – 8.2
Alkalinity, mg/L as CaCO3	150 – 240
Turbidity, NTU	0.9 – 3.4
UV-254, cm^{-1}	0.152 – 0.204
THMFP, µg/L	340 - 460

2.1.2 Experimental Systems. Three experimental systems were used in this project for the evaluation of DBP precursor removal. The operating systems consisted of the ozonation/FBT system, the bench-scale ozonation system, and the biodegradability system. The ozonation/FBT system was used for the evaluation of the removal of THM and other DBP precursors present in drinking water. The bench-scale ozonation system was used for the study of ozonation kinetics. The biodegradability system was used to study the biodegradability potential in the system. Both the ozonation/FBT system and the bench-scale ozonation system used their own ozone generator, mass flow controller, and ozone destruction unit. Both systems, adjacent to one another, shared a Milton Roy Spectronic Genesis-5 spectrophotometer (Milton Roy, Inc., Rochester, NY), and an Orbisphere Laboratories MOCA ozone analyzer (Orbisphere Laboratories, Geneva, Switzerland), which measured ozone concentrations in gas and water, respectively.

2.1.2.1 Ozonation/FBT system. The ozonation/FBT system included an ozone contactor, a retention tank, and a fluidized bed reactor (Figure 2.1). The raw water was pumped from a 15- or 20- gallon barrel using a peristaltic pump into a 1 L ozone contactor. The ozone contactor operates as a downflow injector-type bubble contactor that has a high efficiency for the absorption of ozone [27]. Water and ozone enriched oxygen were pumped into the top of the contactor and flow simultaneously downward through the vertical tube into an expanding cross-section hood, and exited at the base of the contactor. The bubbles inside the ozone contactor were trapped within the hood due to an inlet velocity that was higher than the buoyant velocity of the bubbles, and an exit velocity that was lower than the buoyant velocity of the bubbles. The gas-liquid interfacial area and gas transfer rate and dissolution efficiency were very high due to this.

The materials used for ozonation consisted of glass, stainless steel, PTFE piping, and Teflon® tubing.

The ozone contactor absorbed ozone generated from pure, dry oxygen using an Ozotech Model OZ1PCS/V ozone generator (Ozotech, Inc., Yreka, CA). A Sierra Instrument Model 900 mass flow controller (Sierra Instruments, Inc., Monterey, CA) controlled the gas flow rate to the reactor. This mass flow controller was located between the ozone generator and the ozone contactor. A check valve downstream of the mass flow controller ensured that water could not recycle back into the flow controller. The influent and the effluent ozone gas concentrations were measured spectrophotometrically using a Milton Roy Spectronic Genesys-5 spectrophotometer (Milton Roy, Inc., Rochester, NY) and aqueous ozone concentrations were measured amperimetrically with an Orbisphere MOCA ozone analyzer (Orbisphere Laboratories, Geneva, Switzerland).

The ozonated water entered a glass retention tank by means of a pressure head that develops in the hood of the ozone contactor. The retention tank allowed enough time for the ozone to react with the NOM and provided ozonated samples to be collected for analysis. The retention tank also provided a means for gas to be released when it accumulated in the ozone contactor.

Following the retention tank, water flowed into an equalization tank by means of gravity from which it was pumped through the FBT column at a sufficient rate to fluidize the bed. The media used in the FBR was a non-activated carbon source called Baker product (Calgon Carbon Corporation, Pittsburg, PA). The glass column in the FBT system had a 2 inch diameter and height of 60 inches; the fluidized bed height was maintained at 40 inches.

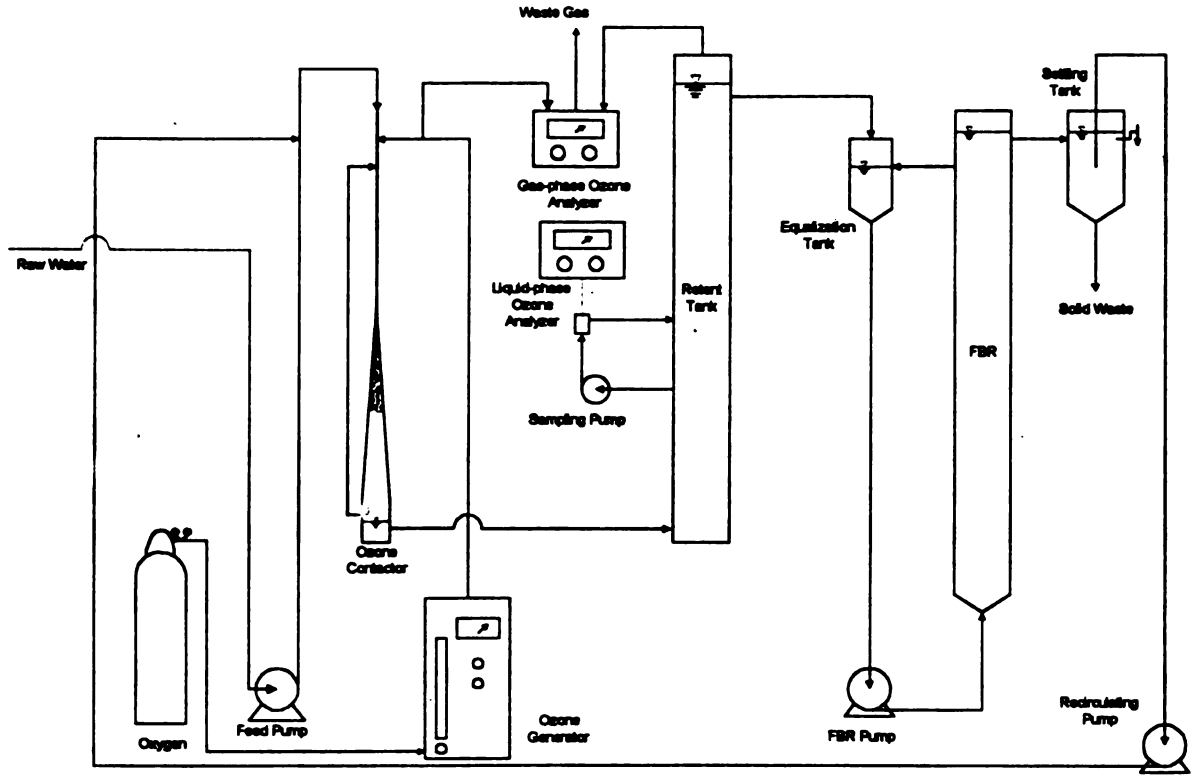


Figure 2.1. Schematic of the Ozonation/FBT System.

After significant research had been conducted on the ozonation/FBT system, it was modified to a FBT/ozonation/biofiltration system. The modified system can be seen in Figure 2.2.

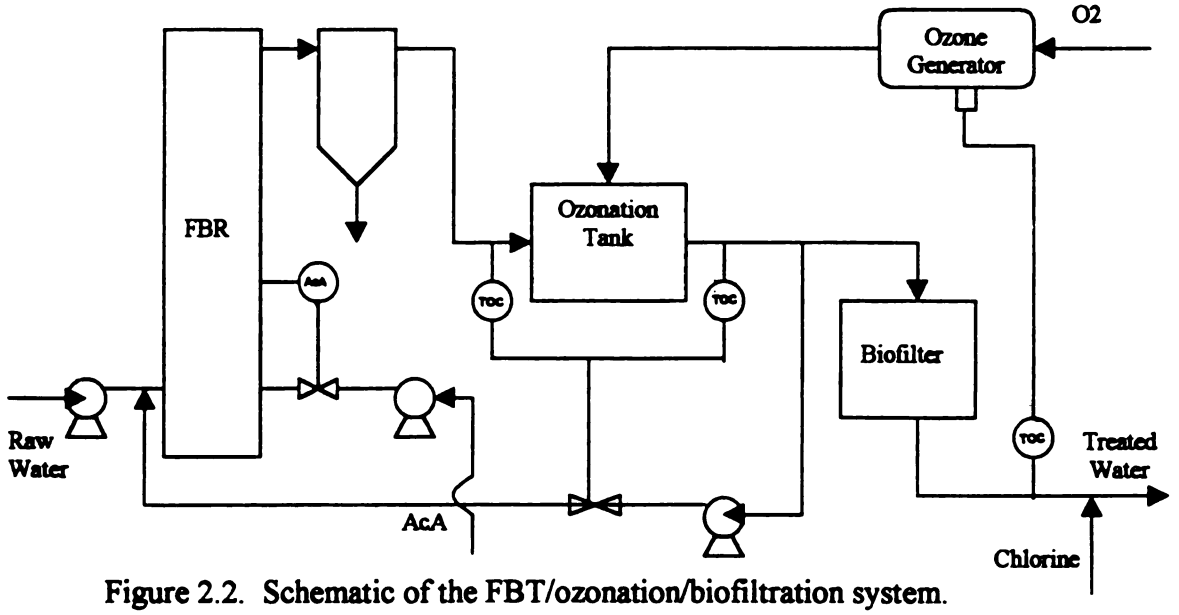


Figure 2.2. Schematic of the FBT/ozonation/biofiltration system.

2.1.2.2 Bench-scale ozonation system. With the bench-scale ozonation system, used for the kinetic studies of ozonation, water samples were pumped into an ozone contactor (Figure 2.3). A mixture of ozone and oxygen was sparged into a 365 mL gas-washing bottle through a fritted glass gas diffuser used as the ozone contactor. The contactor contained approximately 360 mL of water and 5 mL of headspace. This ozone contactor was jacketed for temperature control. The ozone reactor was also equipped with a vent-gas exit port, and water entrance and exit ports. The ozone reactor was operated as a CSTR. All of the fittings and tubing were either PTFE or stainless steel.

The pump downstream of the ozone reactor was operated at the same rate as the inlet pump in order to maintain a constant liquid level in the ozone contactor. The indigo method (Standard Methods, 19th Edition 1995, Method 4500 - O_3 B) was used for any required dissolved ozone measurements in the effluent from the ozone reactor.

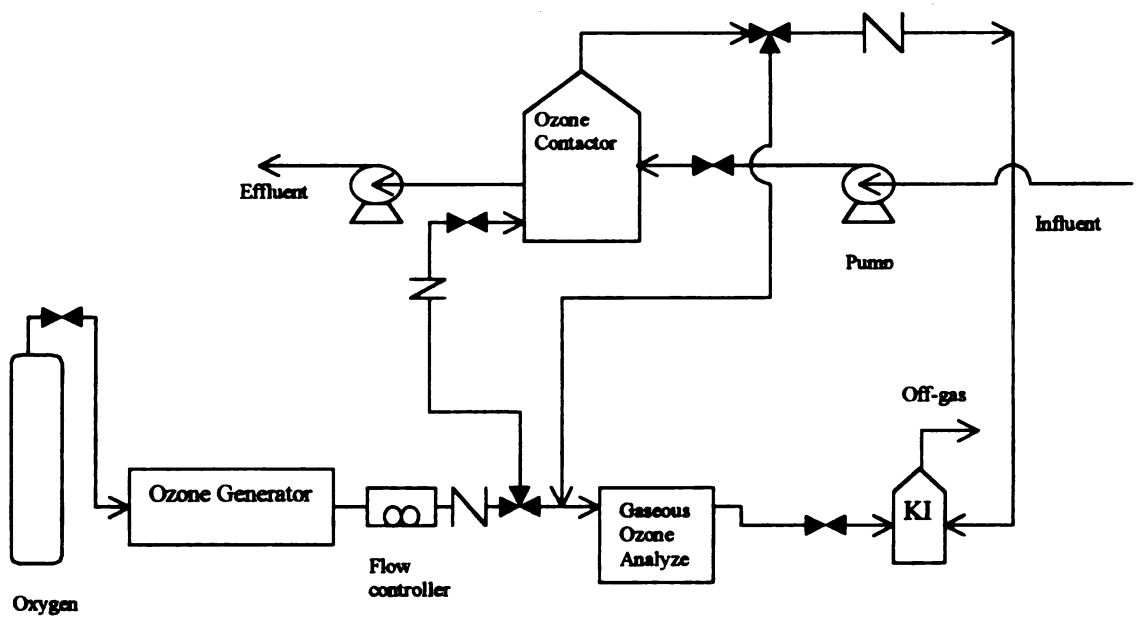


Figure 2.3. Schematic of the bench-scale ozonation system.

The ozone used in the bench-scale ozonation system was also generated using pure, dry oxygen from an Ozotech Model OZ1PCS/V ozone generator (Ozotech, Inc. Yreka, CA). A Sierra Instrument Model 900 mass flow controller (Sierra Instruments, Inc., Monterey, CA) was used to control the gas flow rate in the ozone reactor, and the influent and effluent ozone gas concentrations were monitored using a Milton Roy Spectronic Genesys-5 spectrophotometer (Milton Roy, Inc., Rochester, NY). The indigo method was also used to measure aqueous ozone concentrations in the influent and effluent of the ozone reactor (Standard Methods, 19th Edition 1995, Method 4500–O_3 B).

*2.1.2.3 **Biodegradability System.*** In the biodegradability system, used for the study of biodegradability potential and biodegradability kinetics, water was pumped through a biocolumn. The column used in this system was 20 cm tall with a 1 inch diameter, and had an empty bed volume of 100 mL. The media used in the biodegradability study was a non-activated carbon source called Baker product (Calgon Corporation, Pittsburg, PA). A peristaltic pump was used to maintain a constant downflow through the column at a rate of 2-20 mL/min. Four liters of sample were recirculated through the biocolumn for seven days; samples were taken daily for TOC analysis.

2.2 Analytical Methods

Membrane ultrafiltration was used to characterize the apparent molecular weight distribution of NOM in water samples taken at different stages in the treatment process. Water samples were processed through Amicon Model 8200 ultrafiltration stirred cells containing Amicon YM and YC series ultrafiltration membranes (Amicon, Inc., Danvers,

Massachusetts). The apparent molecular weight cutoffs of the membranes used were 500, 1000, 3000, 10,000, and 30,000 daltons. These membranes are hydrophilic, made of cellulose acetate, and manufactured to exhibit low protein-binding properties [22]. According to the information supplied by Amicon, the rejection efficiency is higher than 98% for compounds greater than the nominal molecular weight cutoff of the specified membranes [28].

Five, 200 mL ultrafiltration stirred cells were operated in parallel, each containing a different series ultrafiltration membrane. All experiments were conducted at room temperature. The cells were pressurized to 55 psi using nitrogen. For continuous mode operation, the stirred cells were connected to a pressurized Amicon Model RG5 five-liter fiberglass reservoir (Amicon, Inc., Danvers, Massachusetts). For batch mode operation, the stirred cells were connected directly to the nitrogen cylinder. A push-button manifold was used for instantaneous direction of gas in multi-cell batch mode or of liquid flow in multi-cell continuous mode (Figures 2.4 and 2.5).

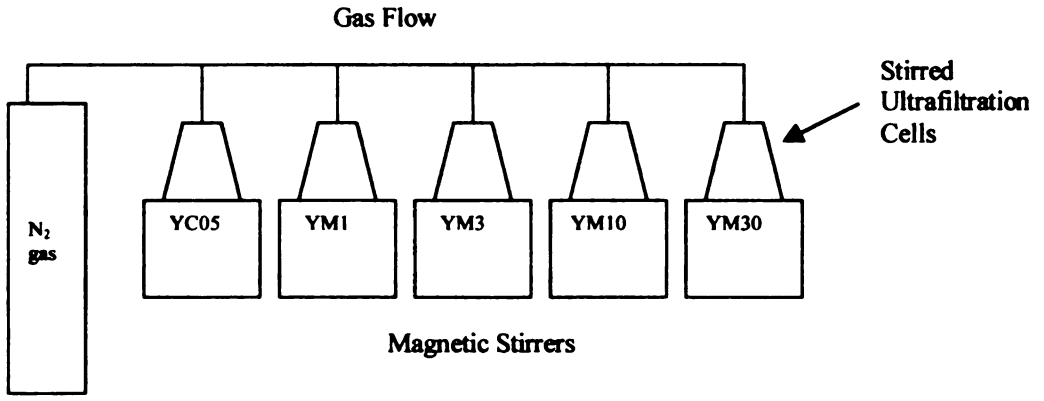


Figure 2.4. Schematic of the batch mode ultrafiltration system.

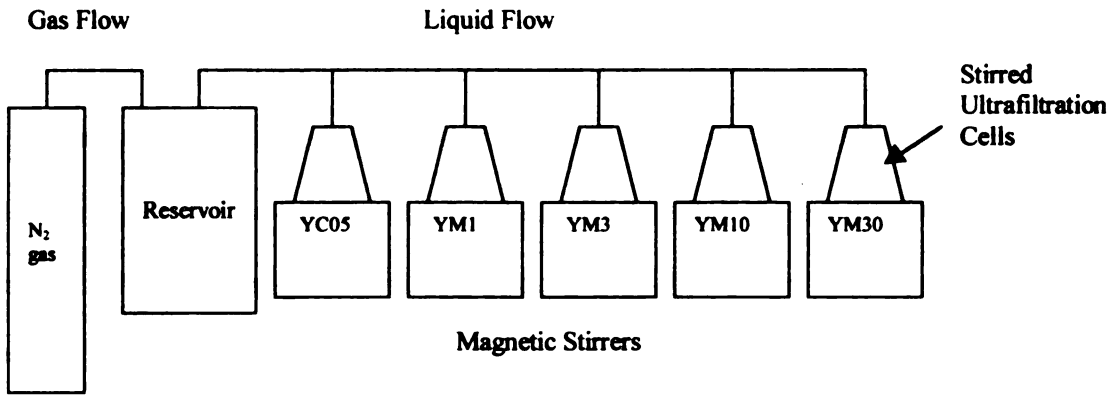


Figure 2.5. Schematic of the continuous mode ultrafiltration system.

Samples were processed through each of the series of membranes to yield a permeate which consisted of material having a molecular weight less than the stated molecular weight cutoff of the membrane. The permeate samples were collected and then analyzed for organic carbon by the USEPA-approved persulfate oxidation method (Standard Methods, 1995, Method 5310 C.) using a Dohrmann DC-190 (Rosemount Analytical, Dohrmann Division, Santa Clara, California) or an O.I. Analytical Model 1010 (O.I. Analytical, College Station, Texas) wet oxidation total organic carbon (TOC) analyzer. Triplicate measurements were made for each sample, and standard deviations were calculated for a 95% confidence level.

Several factors were taken into consideration to determine the volume of sample that should be collected for analysis to best represent the characteristics of the water present in the actual systems. The following preliminary experiments were conducted to establish a protocol for the apparent molecular weight distribution study.

2.2.1 Batch Mode Experiments. Water samples were processed through the ultrafiltration membranes in batch mode and two permeate samples were collected at different volumes to determine the effect of volume eluted on TOC concentration. The first forty milliliters of permeate were discarded to eliminate any dilution effects on the sample. Permeate samples were collected from 40-80 ml, and 80-120 ml aliquots. The samples were then analyzed for TOC concentration. The objective of this experiment was to determine the effects of increasing volume on the absolute TOC measurements at the two volumes, and on the trends of the NOM in the samples throughout the stages of the treatment process.

2.2.2 Batch Mode vs Continuous Mode. Experiments were also conducted in which untreated Huron River water was processed using the continuous mode ultrafiltration system. The continuous mode procedure was conducted with the use of a pressurized reservoir to maintain a constant volume within the ultrafiltration cells. The first forty milliliters of permeate were discarded, and sample volumes from 40-80 mL, and from 80-120 mL were then collected. Both samples were collected from a continuous 200 mL sample that was processed through all five of the ultrafiltration membranes. The TOC results from this experiment were compared to the results obtained from the untreated water sample described above in the batch mode experiment.

2.2.3 Continuous Mode – 400 mL Samples. Additional ultrafiltration experiments were conducted on untreated Huron River water to determine the effect of increasing volumes on the TOC concentrations of samples processed in continuous mode. The objective was to evaluate the TOC concentrations of samples collected during a during a continuous 400 mL process. Five 40 mL samples from 40-80 mL, 120-160 mL,

200-240 mL, 280-320 mL, and 360-400 mL were collected as 400 mL of sample was passed through each membrane. Samples from 0-40 mL, 80-120 mL, 160-200 mL, 240-280 mL and 320-360 mL were discarded.

2.2.4 Continuous Mode – Raw Huron River vs Biocolumn Effluent Samples. Experiments were conducted to investigate the TOC concentrations at increasing permeate volumes using two samples of different concentrations. It was suspected that the effect of increasing sample volume on TOC concentration would be more profound in highly concentrated samples. Two experiments were conducted in which raw Huron River water was compared to seven-day biocolumn effluent. Samples were processed through a continuous mode ultrafiltration system with the use of a reservoir. Five, 40 mL samples were collected using the 200 mL of each water type that was processed through the ultrafiltration cell.

2.2.5 Continuous Mode – 100 mL composite vs 150 mL composite Sample. Further apparent molecular weight distribution experiments were conducted to investigate the differences in TOC concentration in a 100 mL composite sample compared to a 150 mL composite sample. Each composite sample was collected in a 150 mL flask in which a 40 mL sample was taken for TOC analysis. The apparent molecular weight distribution of untreated Huron River water and ozonation/FBT effluent water was determined at both sample volumes. These samples were processed using continuous mode in which the first 20 mL were discarded and then the composite sample was collected.

2.3 Results and Discussion

2.3.1 Batch Mode Experiments. Results listed in Table 2.2 show that the absolute TOC concentration increased as the permeate volume increased. The ultrafiltration membranes display an increase in the TOC concentration when comparing the 40-80 ml sample to the 80-120 ml sample (Table 2.2). These results indicate that as the volume of the permeate increases, the TOC concentration of the permeate also increases. However, the increase in TOC is more significant for membranes with lower molecular weight cutoffs. The results in Table 2.2 show that there is no significant change in TOC in the samples passed through the YM30 membrane.

Table 2.2. TOC concentration as a function of increasing sample volume.

		TOC Concentration (mg/L)				
Sample	**Volume (mL)**	**YC05**	**YM1**	**YM3**	**YM10**	**YM30**
Raw Water	40-80	0.39	1.03	2.8	4.45	5.66
Sample	80-120	0.48	1.52	3.48	5.03	5.73
Ozonated	40-80	0.38	1.12	2.63	3.87	4.86
Sample	80-120	0.47	1.60	3.32	4.33	4.89
Ozone/FBR	40-80	0.36	0.88	2.20	3.33	4.18
Effluent	80-120	0.44	1.35	2.79	3.81	4.17

*Note: The ozonation/FBT system was operated at an ozone dose of 1.0 mg/mg C.

In this batch mode experiment, the feed volume in the stirred cells decreased as the sample passed through the membrane. This is thought to cause the concentration differential across the membrane to increase. Since the flux of the solute through the ultrafiltration membrane is directly proportional to the concentration gradient across the membrane [4], it was expected that the TOC concentration would increase linearly as the feed concentration increased. Therefore, as the permeate volume increased, the flux of

solutes through the membrane also increased which caused the TOC concentration in the permeate to increase. These results are consistent with previous studies which found that as the permeate volume increased and the feed concentration increased, the retention of solute decreased [29]. Macko et al. also found that the filtrate concentration increased linearly with feed concentration [30]. Another possible reason for the increase in TOC concentration is concentration polarization [22].

The results shown in Table 2.2 were used to plot the TOC concentrations of the different molecular weight fractions in samples collected at different stages in the treatment processes (Figures 2.6 and 2.7). It can be seen that while the increasing volume may have a major impact on the absolute values of TOC for each membrane, no significant effect on the trends for each process were seen (Figures 2.6 and 2.7). Figure 2.6 displays the TOC concentrations for the 40-80 mL sample collected, and Figure 2.7 illustrates the TOC concentrations for the 80-120 mL sample collected. Both samples in Figures 2.6 and 2.7 were taken from the 200 mL volume that was processed through all of the ultrafiltration membranes. Although there was a significant difference in the absolute TOC values for these different volumes (Table 2.2), the same trend can be seen (Figures 2.6 and 2.7) throughout the stages of the treatment process. This result is an indication that the major trends in the apparent molecular weight fractions can be determined from the TOC concentrations measured at varying volumes.

The TOC data for the 40-80 mL and 80-120 mL fractions presented in Figures 2.6 and 2.7 were also compared to the average TOC data for the entire 200 mL sample presented in Figure 2.8. Results show that the trends are exactly the same for the entire 200 mL TOC values compared to the 40-80 mL and 80-120 mL fraction values.

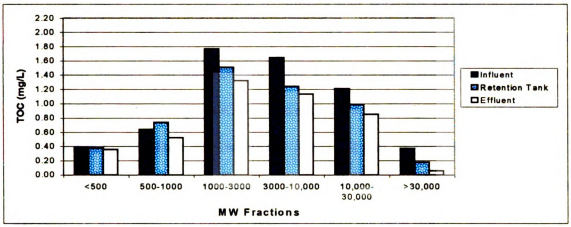


Figure 2.6. TOC concentrations in the 40-80 mL fraction of 200 mL water samples used to evaluate the transformation of NOM during ozonation and biological treatment.

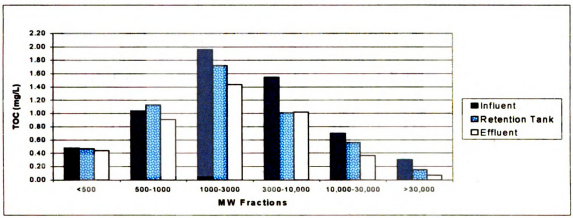


Figure 2.7. TOC concentrations in the 80-120 mL fraction of 200 mL samples used to evaluate the transformation of NOM during ozonation and biological treatment.

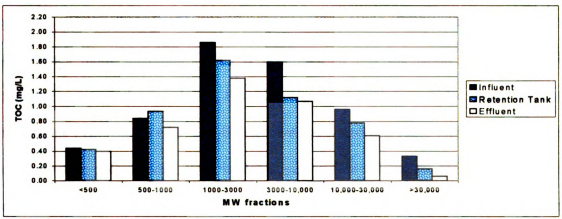


Figure 2.8. TOC concentrations obtained from an average over the entire 200 mL sample used to evaluate the transformation of NOM during ozonation and biological treatment.

Therefore, these results support the hypothesis that although increasing volume may affect the absolute TOC measurements, there will be no effect on the distribution. These results also indicate that the TOC for small 40 mL sample volumes were an accurate representation of the average TOC over the entire 200 mL composite sample volume.

2.3.2 Batch Mode vs Continuous Mode. It can be seen in Table 2.3 that the difference in TOC at increasing volumes is much smaller for the samples processed with the reservoir as compared to those processed without the reservoir.

Table 2.3. TOC values from samples processed in batch and continuous mode.

	Batch Mode TOC Concentrations (mg/L)				Continuous Mode TOC Concentrations (mg/L)		
Membrane	40-80 mL Sample	80-120 mL Sample	Difference	Membrane	40-80 mL Sample	80-120 mL Sample	Difference
YC05	0.39	0.48	0.09	YC05	0.49[1]	0.51	0.02
YM1	1.03	1.52	0.49	YM1	1.09	1.24	0.15
YM3	2.80	3.48	0.68	YM3	2.55	2.68	0.13
YM10	4.45	5.03	0.58	YM10	3.93	4.06	0.13
YM30	5.66	5.73	0.07	YM30	5.25	5.33	0.08
Filtered[2]	6.03	6.03	0.00	Filtered[2]	5.88	5.88	0.00

[1] The higher value of TOC may be attributed to the different batches of water.
[2] The samples were filtered using a 0.45 μm glass fiber filter.

Maintaining a constant volume within the stirred cell caused the concentration gradient across the ultrafiltration membrane to remain fairly constant during the continuous mode operation. This is beneficial in that the larger the concentration gradient is across the membrane, the more rapidly the solute particles move across the membrane [4]. Macko et al. and Brock have suggested that rapid mixing will minimize concentration polarization, and it is also advantageous to keep the feed concentration as dilute as possible [30-31]. This was done by maintaining a constant volume in the stirred cell with the use of the reservoir. Unlike the batch mode system, the reservoir maintained

a relatively stable feed concentration which maintained a relatively stable flux of solute through the ultrafiltration membrane. Therefore, the increase in TOC concentration with increasing permeate volume was much smaller for the continuous mode experiment as compared to the batch mode experiment. These results indicated that processing samples in continuous mode minimizes the effects of increasing permeate volume on the TOC concentration of the sample. All subsequent experiments in this phase were conducted with the use of a reservoir.

2.3.3 Continuous Mode – 400 mL Samples. Results in Figures 2.9-2.13 display TOC concentration as a function of increasing sample volume. Results show that the TOC concentrations progressively increase with volume for every membrane when 400 mL of water is processed (Figures 2.9-2.13).

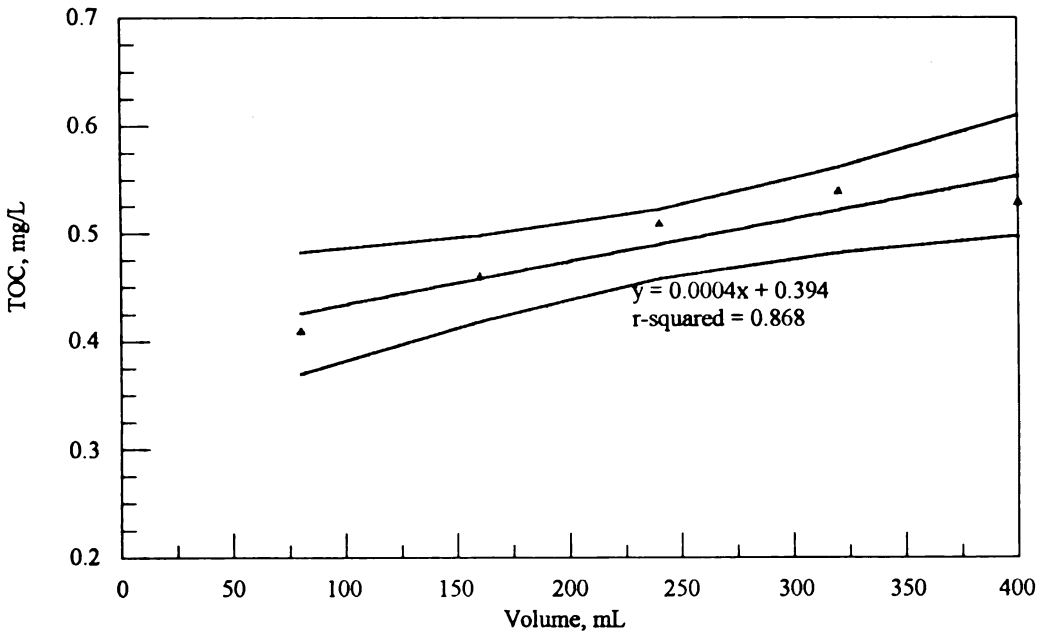


Figure 2.9. TOC concentrations as 400 mL of untreated Huron River water passed through the YC05 ultrafiltration membrane.

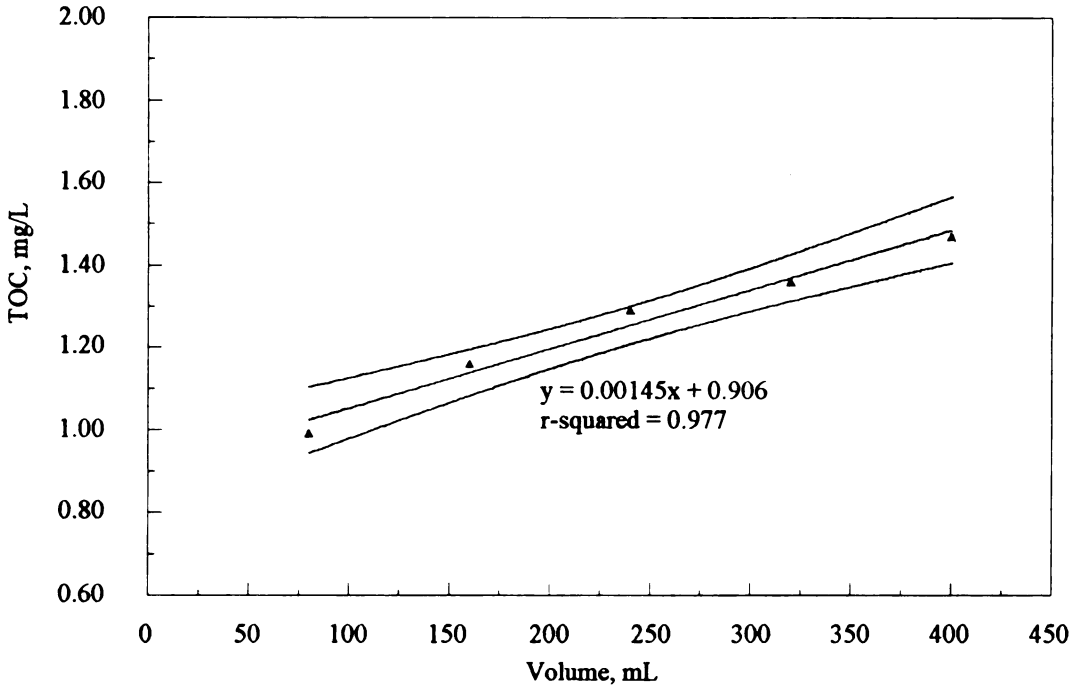


Figure 2.10. TOC concentrations as 400 mL of untreated Huron River water passed through the YM1 membrane.

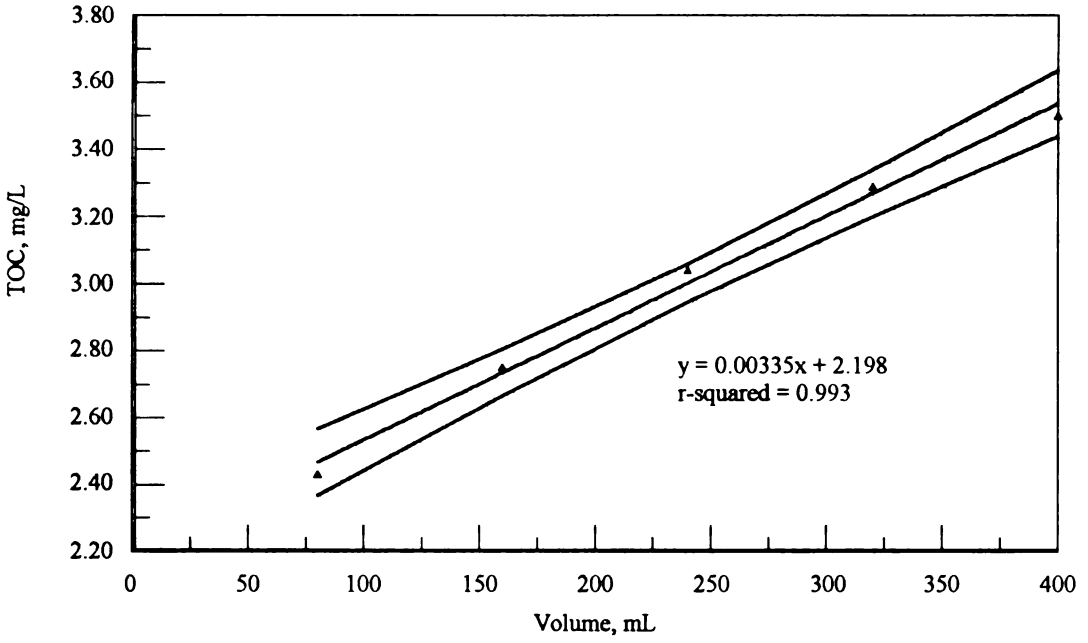


Figure 2.11. TOC concentrations as 400 mL of untreated Huron River water passes through the YM3 membrane.

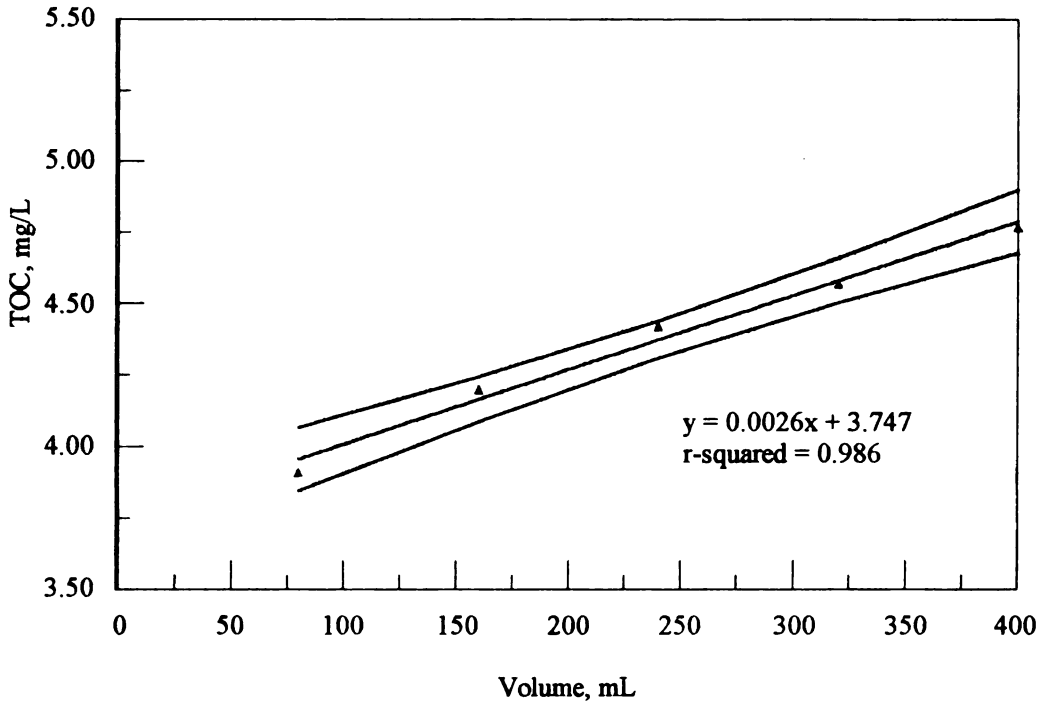


Figure 2.12. TOC concentrations as 400 mL of untreated Huron River water passes through the YM10 membrane.

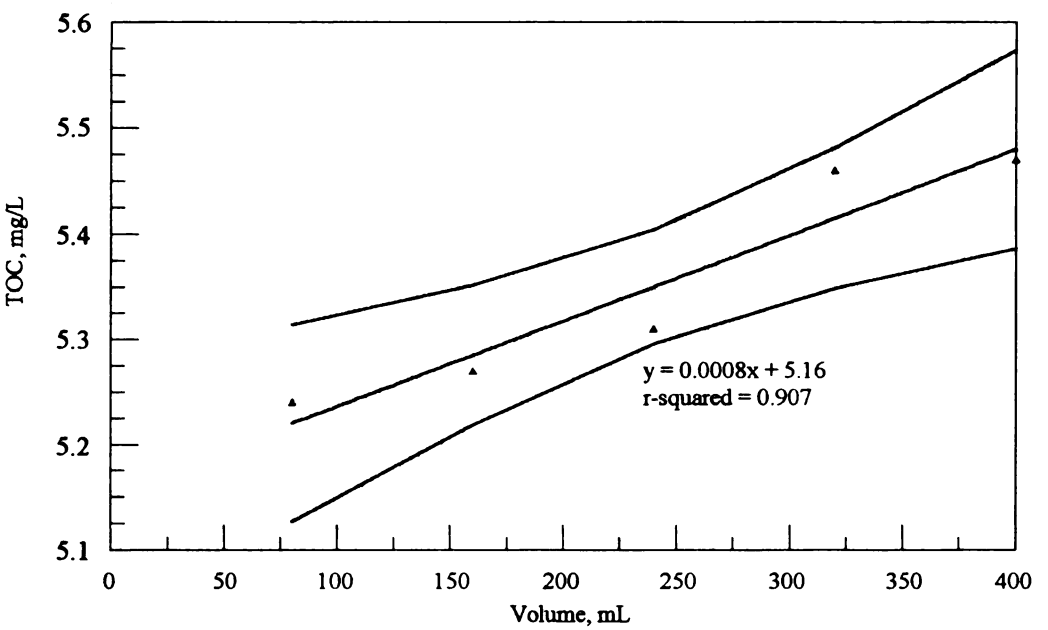


Figure 2.13. TOC concentrations as 400 mL of untreated Huron River water passes through the YM30 membrane.

2.3.4 Continuous Mode – Raw Huron River vs Biocolumn Effluent Samples.

The TOC concentrations of untreated Huron River water and biocolumn effluent water are compared in Figures 2.14-2.18. Results show that the TOC concentrations increase with increasing permeate volume through all of the membranes except for the biocolumn effluent in Figure 2.14. The decrease in slope in the biocolumn effluent through the YC05 membrane may be due to high amounts of error in the linear regression which is shown by the large confidence bands. The 95% confidence interval for the slope indicates that the slope of the biocolumn effluent through the YC05 membrane could be positive or negative (Figure 2.14). Therefore, these results suggest that the decrease in TOC concentration may be due to analytical error.

The results in Figures 2.14-2.18 do not show any systematic trends between the raw Huron River water and the biocolumn effluent water through the different membranes. However, it was shown that the TOC concentrations increased more rapidly for the more concentrated, influent sample than the biocolumn effluent samples. This may be due to a larger concentration gradient across the ultrafiltration membrane for the more concentrated sample. Based on literature, the time for concentration polarization to occur is inversely proportional to concentration, and therefore, it was expected that concentration polarization would occur more quickly for more concentrated samples [22].

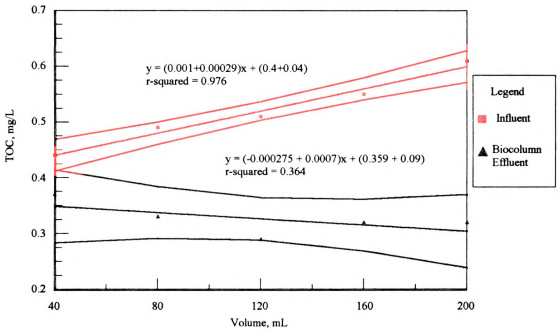


Figure 2.14. TOC concentrations as 200-mL samples pass through the YC05 membrane.

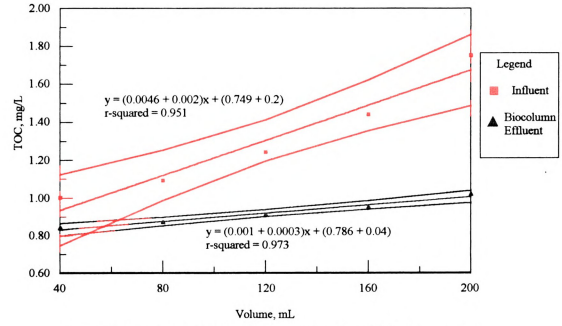


Figure 2.15. TOC concentrations as 200-mL samples pass through the YM1 membrane.

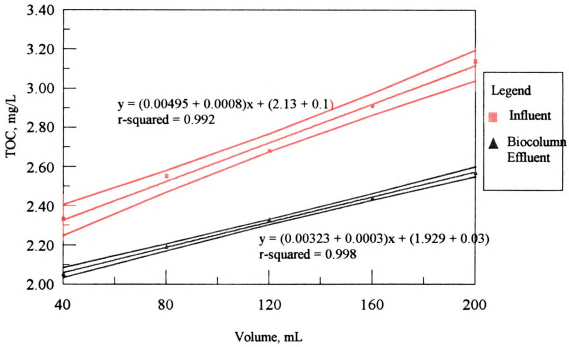


Figure 2.16. TOC concentrations as 200-mL samples pass through the YM3 membrane.

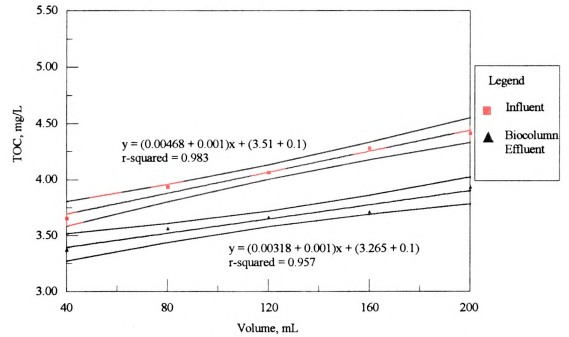


Figure 2.17. TOC concentrations as 200-mL samples pass through the YM10 membrane.

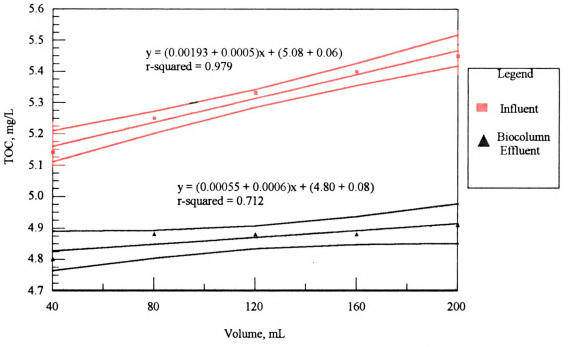


Figure 2.18. TOC concentrations as 200-mL samples pass through the YM30 membrane.

2.3.5 Continuous Mode – 100 mL composite vs 150 mL composite Sample. The apparent molecular weight distribution results for the raw water and ozonation/FBT effluent samples are displayed in Figures 2.19 and 2.20, respectively.

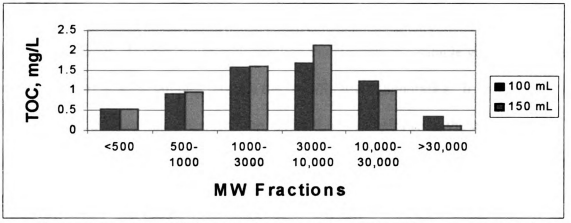


Figure 2.19. TOC of different molecular weight fractions for raw water samples collected at 100 mL and 150 mL.

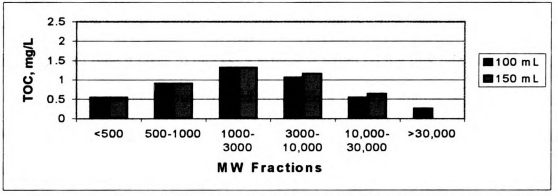


Figure 2.20. TOC of different molecular weight fractions for ozonation/FBT samples collected at 100 mL and 150 mL.

It appeared that there was no change in TOC concentrations in the apparent molecular weight fractions below 3000 daltons for both samples. There were some differences in the measured TOC of higher molecular weight fractions sampled at 100 mL versus 150 mL. There was no obvious trend between the raw water and the ozonation/FBT sample. The difference may be due to experimental error. It was decided

that the 100 mL composite sample volume would be used for the final protocol. Based on the results obtained in the protocol development and the qualitative nature of this apparent molecular weight distribution study, it was concluded that the sample volume would not have an effect on the overall trends as long as a consistent protocol was utilized for all samples being compared.

2.3.6 Time. Another major consideration in determining a sample volume was the time required to process samples through the ultrafiltration membranes. It was necessary to process and analyze influent, ozonation, and effluent samples from the ozonation/FBT system on the same day in order to ensure that the same experimental conditions were applied to all three samples. Ogura [29] suggested that results used for comparative analysis are only reliable when the process is run under the same experimental conditions. Analyzing all of the samples on the same day also ensured that the same calibration curve and operational parameters were used for TOC analysis of the samples. The amount of time it takes to process a sample is based on the flux rate and area of the membrane. The estimated time required to process a 120 mL volume of sample through each membrane, based on the manufacturer's information and observed data using purchased membranes, is presented in Table 2.4.

Table 2.4. Time required to process 120 mL through ultrafiltration membranes.

Membrane	Volume (mL)	Time required (Approximated)
YM30	120	4 – 5 min
YM10	120	20 min
YM3	120	70 min
YM1	120	105 min – 120 min
YC05	120	105 min – 120 min

Approximately two hours is required to process 120 mL through the YC05 and YM1 membranes, which have the smallest apparent molecular weight cutoff. Therefore, it took approximately six hours to process all three samples through the ultrafiltration membranes. The overall procedure required approximately ten hours including the time to collect the sample, prefilter it, process it through the membranes, clean the equipment, and restore the membranes for further use. A 120 mL sample was, therefore, considered a practical volume for processing three samples in the same day.

2.4 Conclusions and Final Protocol Selection

Apparent molecular weight distribution was used for comparative analysis rather than for quantifying data. Increasing sample volumes beyond 120 mL did not effect the trends in TOC concentration for raw and treated water. Based on the results from these experiments and literature on related research [23,32], the following protocol was developed:

- Prior to ultrafiltration all samples were filtered through 0.45 μm glass fiber filters to avoid membrane damage from the particulates in the sample.
- Each ultrafiltration cell was completely filled with the water sample, placed on a magnetic stirring table and stirred at a constant rate to reduce the concentration polarization.
- The cells were pressurized with nitrogen gas at 55 psi. The samples were forced through the ultrafiltraion cells, each containing a different membrane.
- The first 20 ml of permeate were discarded to avoid dilution effects from the rinse water on the membrane.

- 100 mL composite samples were collected for analysis.
- The same procedure was repeated for influent, ozonation, and effluent samples on the same day. Results allowed for the comparative analysis of all samples processed under the same operational and analytical conditions.
- The following instructions were given by the membrane manufacturer [28], for proper care of the ultrafiltration membranes to achieve accurate results:
    - Soak new membranes in deionized water for one hour for removal of glycerin or sodium azide used to preserve the membranes.
    - Soak all YM membranes in 0.1 N NaOH, and YC05 membranes in 1.0 M NaCl for thirty minutes between sample runs for restoration of the membranes.
    - Store all membranes in <10% ethanol/water solution and refrigerated for reuse.
    - Replace membranes every eight to ten sample runs.

Also, the reservoir ensured that the same samples were processed simultaneously through all five membranes without a decreased volume in the stirred ultrafiltration cells.

Once this protocol was established, triplicate experiments were conducted to determine the standard deviation. The error differed for each apparent molecular weight fraction. The following tables show the typical standard deviations for all apparent molecular weight fractions in a raw water sample and an FBT/ozonation effluent sample using the established protocol. The results show that the standard deviation did not exceed 10% for all apparent molecular weight fractions less than 10,000 daltons. These fractions averaged a relative standard deviation of 3.8%. However, the standard deviation is significantly larger for the apparent molecular weight compounds greater than 10,000 daltons. This can be attributed to very low concentrations in these fractions.

Therefore, the larger error needs to be taken into account when making any conclusions on the higher apparent molecular weight fractions.

Table 2.5. Standard Deviations for a raw water sample processed in triplicate using the established protocol.

	TOC (mg/L)					
Apparent MW Fraction	Run 1	Run 2	Run 3	Average	Std Dev	Relative Std Dev (%)
<500	0.26	0.28	0.28	0.28	0.02	7.14
500-1000	0.67	0.66	0.66	0.66	0.02	3.03
1000-3000	1.95	1.90	1.90	1.93	0.02	1.04
3000-10,000	1.53	1.63	1.63	1.61	0.07	4.35
10,000-30,000	1.45	1.48	1.48	1.45	0.08	5.52
>30,000	0.54	0.40	0.40	0.59	0.24	40.7

Table 2.6. Standard Deviation for an FBT/ozonation sample processed in triplicate using the established protocol.

	TOC (mg/L)					
Apparent MW Fraction	Run 1	Run 2	Run 3	Average	Std Dev	Relative Std Dev (%)
<500	0.38	0.43	0.43	0.41	0.03	7.32
500-1000	1.10	1.06	1.08	1.08	0.03	2.78
1000-3000	1.60	1.62	1.62	1.61	0.03	1.86
3000-10,000	1.08	1.06	1.04	1.06	0.03	2.83
10,000-30,000	0.81	0.87	1.00	0.89	0.10	11.2
>30,000	0.18	0.09	0.11	0.13	0.13	100

CHAPTER 3

PHASE II – EFFECT OF TREATMENT METHODS ON NOM BASED ON APPARENT MOLECULAR WEIGHT DISTRIBUTION AND TOC REMOVAL

3.1 Methodology

3.1.1 Effect of FBR Treatment on Apparent Molecular Weight Distribution. Experiments were conducted to determine the effect of biological treatment on TOC removal in different apparent molecular weight fractions. The FBT system was operated at a flow rate of 0.6 L/hr, which produced an empty-bed contact time (EBCT) of 180 minutes. Samples were collected before and after fluidized bed treatment at an ozone dose of zero. Samples were processed through five different ultrafiltration membranes to determine the apparent molecular weight distribution. The TOC of each fraction was measured to evaluate the extent to which the organic matter of each apparent molecular weight fraction was transformed due to biodegradation. All experiments were conducted at room temperature.

3.1.2 Effect of Ozonation/FBT on Apparent Molecular Weight Distribution. The FBT in the ozonation/FBT system was operated under the same experimental conditions as described in the previous section. The effect of ozone dose was investigated for the removal of NOM by the ozonation/FBT process. Ozone dosages of 0.5, 1.0, 2.0, and 7 mg/mg C were examined.

3.1.3 Effect of Ozonation/FBT on TOC Removal in Unfractionated Samples. The transformation of NOM was also evaluated throughout the treatment stages using TOC concentrations of unfractionated samples. The removal of TOC in unfractionated

samples during the ozonation/FBT was compared to the results obtained in the apparent molecular weight distribution studies. The TOC removal in unfractionated samples was evaluated to test the hypothesis that ozone increased the efficiency of the FBT at doses higher than 1.0 mg/mg C. Ozone dosages of 0, 0.5, 1.0, 2.0, and 7 mg/mg C were examined.

3.1.4 Effect of FBT/ozonation on the Apparent Molecular Weight Distribution. To further increase the treatment efficiency, the treatment train was modified to allow FBT to be the initial stage followed by ozonation, with the recycle of a portion of ozonation effluent to the FBT column. The goal of the FBT/ozonation system was to ensure that ozone was used for the production of biodegradable organic carbon rather than for the oxidation of organic carbon that could otherwise be removed by biological treatment. Therefore, it was expected that the FBT would remove the biodegradable organic carbon, and ozone would increase the biodegradable organic carbon concentration in samples to be recycled back to the FBT system.

3.2 Results and Discussion

3.2.1 Effect of FBR Treatment. It was expected that biodegradation occurring during FBT would remove the lower molecular weight compounds (<1000 daltons), and have no significant effect on the higher molecular weight compounds. Goel [14], suggested that lower molecular weight compounds are more biodegradable due to easier mass transfer across the cell membrane, and greater accessibility to metabolic enzyme attack.

The TOC concentrations of the apparent molecular weight fractions before and after the FBT are shown in Figure 3.1.

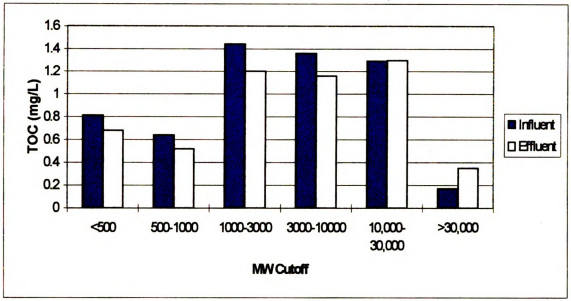


Figure 3.1. Effect of the FBT on apparent molecular weight distribution.

The results indicate that there was some removal of both high and low molecular weight compounds. Surprisingly, FBT removed the higher molecular weight compounds as well as the lower molecular weight compounds. These results indicate that either the lower molecular weight compounds were not a good carbon source for the microorganisms in the FBR, or the higher molecular weight compounds were being broken down into lower molecular weight compounds, resulting in no significant net change in the TOC of the lower molecular weight fraction.

It should be noted that the removal of higher molecular weight compounds was not entirely due to sorption or charge-binding effects since no breakthrough of organic matter was seen in the nine months of operation, and a nonsorbing material was used as the biomass carrier in the FBR. The removal of higher molecular weight compounds was

possibly due to enzymes that were attached to the outer surface of the cell membrane. However, there was no significant change in the molecular weight compounds between 10,000 and 30,000 daltons, and there was an increase in the compounds greater than 30,000 daltons. The increase in the compounds greater than 30,000 daltons was an unexpected result and may be due to a release of extracellular polymers during the growth and decay of microorganisms [33]. This is especially true in starved conditions in the FBR.

3.2.2 Effect of Ozonation/FBT at an Ozone Dose of 0.5 mg/mg C. An ozone dose of 0.5 mg/mg C was applied to the ozonation/FBT system. It was expected that at this dosage, the ozonated water would be more biodegradable than untreated Huron River water, and the ozone would consequently increase the FBT efficiency. Due to the increase in lower molecular weight compounds, it was expected that during FBT, the removal of NOM in ozonated water would be higher than the removal of NOM in untreated river water. Figure 3.2 displays the TOC removal achieved at an ozone dose of 0.5 mg/mg C.

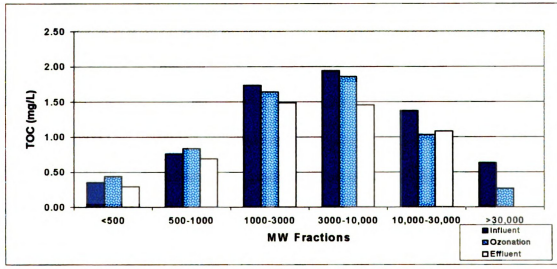


Figure 3.2. Effect of the ozonation/FBT system at an ozone dose of 0.5 mg/mg C.

As expected, the results in Figure 3.2 show that ozonation decreased the concentration of higher molecular weight compounds. Surprisingly, there was not a corresponding increase in the lower molecular weight compounds. These results suggest that the ozone simultaneously oxidized both high and low molecular weight compounds. Therefore, an ozone dose of 0.5 mg/mg C did not significantly improve the biodegradability of organic matter in the samples since the ozone did not increase the amount of low molecular weight substrate available for biodegradation in the FBR. This observation is supported by the apparent molecular weight distribution after FBT. Similar trends in the removal of TOC during FBT can be seen for raw water (Figure 3.1) and ozonated water (Figure 3.2). In both cases, there was removal of lower and higher molecular weight compounds by biodegradation. Once again, these results suggest that the low molecular weight compounds were not a good substrate for the microorganisms in the FBR, or the microorganisms were breaking the higher molecular weight compounds down into smaller molecular weight compounds. Therefore, the addition of ozone at a dose of 0.5 mg/mg C did not increase the biodegradation in the samples, and the FBT system alone would achieve similar biodegradation results as the combined ozonation/FBT system with an ozone dose of 0.5 mg/mg C.

3.2.3 Effect of Ozonation/FBT at an Ozone Dose of 1.0 mg/mg C. The ozone dose in the ozonation/FBT system was increased to 1.0 mg/mg C to investigate the removal of NOM by combined ozonation and biological treatment at a higher ozone dose. The ozone again was expected to produce more biodegradable water for FBT by oxidizing higher molecular weight compounds into lower molecular weight compounds.

Figure 3.3 illustrates the apparent molecular weight distribution of NOM throughout the ozonation/FBT system at an ozone dose of 1.0 mg/mg C.

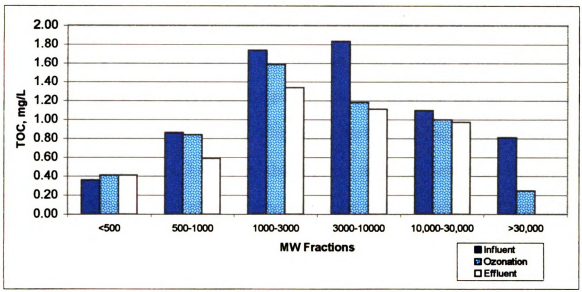


Figure 3.3. Effect of the ozonation/FBT system at an ozone dose of 1.0 mg/mg C.

Results show that the removal of higher molecular weight compounds by ozonation is greater with an ozone dose of 1.0 mg/mg C as compared to the ozone dose of 0.5 mg/mg C. As expected, all of the higher molecular weight fractions were reduced, but the higher ozone dose still did not increase the concentration of smaller molecular weight compounds (<1000 daltons). Therefore, the results of ozonation at an ozone dose of 1.0 mg/mg C are consistent with the results of ozonation at an ozone dose of 0.5 mg/mg C. The ozone simultaneously oxidized the low and high molecular weight fractions at ozone dosages of 0.5 mg/mg C and 1.0 mg/mg C.

Also, there was no major difference in the apparent molecular weight distribution of FBT samples at ozone doses 0, 0.5, and 1.0 mg/mg C (Figures 3.1-3.3). Results

showed some removal of both high and low molecular weight compounds at all three ozone dosages.

3.2.4 Effect of Ozonation/FBT at an Ozone Dose of 2.0 mg/mg C. The ozone dose was further increased to 2.0 mg/mg C in the ozonation/FBT system to investigate the effects of a higher ozone dosage on the transformation of NOM. It was hypothesized that at this high dose, ozone would be more effective at oxidizing the higher molecular weight compounds into the lower, more biodegradable organic compounds.

Results in Figure 3.4 display the apparent molecular weight fractionation of samples at different stages of the treatment processes in the ozonation/FBT system with an ozone dose of 2.0 mg/mg C.

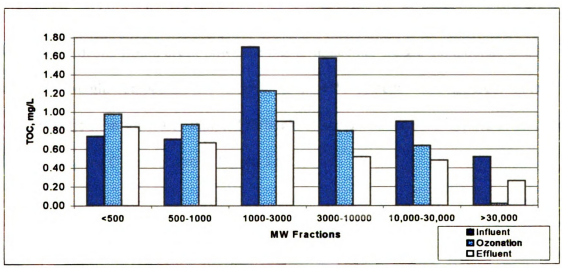


Figure 3.4. Effect of the ozonation/FBT system at an ozone dose of 2.0 mg/mg C.

The results obtained using an ozone dose of 2.0 mg/mg C displayed a different apparent molecular weight distribution than at ozone doses of 0.5 and 1.0 mg/mg C. As expected, the removal of higher molecular weight compounds was greater at the ozone dose of 2.0 mg/mg C than at the lower ozone doses, but unlike the results from ozone doses 0.5 and 1.0 mg/mg C, the higher ozone dose caused an increase in the concentration of the

compounds having an apparent molecular weight less than 1000 daltons. It appears that the concentrations of all apparent molecular weight fractions were reduced after FBT. The higher ozone dose increased the TOC in the fractions containing the lower molecular weight compounds, but the microorganisms in the FBT continued to break down both high and low molecular weight compounds.

3.2.5 Effect of Ozonation/FBT at an Ozone Dose of ~7 mg/mg C. To show the maximum effect of ozone on NOM, the ozonation/FBT system was operated at an extremely high ozone dosage of approximately 7 mg/mg C. It is important to note that such a high ozone dosage would not be feasible for full-scale systems, but in pilot-scale studies, the high ozone dose displays the extreme effect of ozone on the apparent molecular weight distribution throughout the treatment processes. The expected result was that the ozone would break down the higher molecular weight compounds into lower molecular weight compounds for removal in the FBT system. The apparent molecular weight distribution for water sampled throughout the ozonation/FBT system at an ozone dose of 7 mg/mg C can be seen in Figure 3.5.

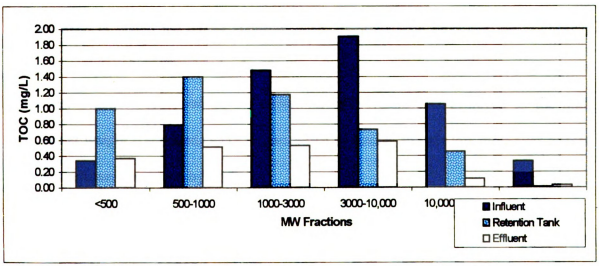


Figure 3.5. Effect of the ozonation/FBT system at an ozone dose ~7 mg/mg C.

It can be clearly seen in Figure 3.5 that the results are as expected. After ozonation, there was a tremendous decrease in the concentration of the compounds having a molecular weight greater than 1000 daltons, and a tremendous increase in the concentration of the compounds having a molecular weight less than 1000 daltons. This is the same trend that can be seen in Figure 3.4, when the system was operating at an ozone dose of 2.0 mg/mg C, but the changes are more dramatic at the higher ozone dose of 7 mg/mg C. These results indicate that the high molecular weight compounds were broken down more efficiently at higher ozone dosages thereby increasing the potential for biodegradability in the FBT.

The results also show that the TOC of all of the molecular weight fractions, except the highest molecular weight fraction, decreased considerably after FBT. The TOC of the highest apparent molecular weight fraction did not show any major change (Figure 3.5). The only substantial removal of TOC in the lower apparent molecular weight fraction by FBT occurred at an ozone dose of 7 mg/mg C. These results indicate that the FBT efficiency improved at a higher ozone dose as more biodegradable organic compounds were produced. However, the FBT efficiency was not affected by the lower ozone dose in which the ozone simultaneously oxidized both high and low molecular weight compounds. The results in Figure 3.5 provided evidence that at high ozone dosages, desirable operation of the ozonation/FBT system was achieved as the high molecular weight compounds were broken down by ozone, and the low molecular weight compounds were removed by FBT.

3.2.6 TOC Removal in Unfractionated Samples by Ozonation/FBT. The TOC in unfractionated samples was used as another surrogate parameter to evaluate the

ozonation/FBT system. The TOC results obtained from unfractionated samples (Figure 3.6) were compared to TOC results obtained from the apparent molecular weight distribution of other samples at varying ozone dosages (Figures 3.1-3.5).

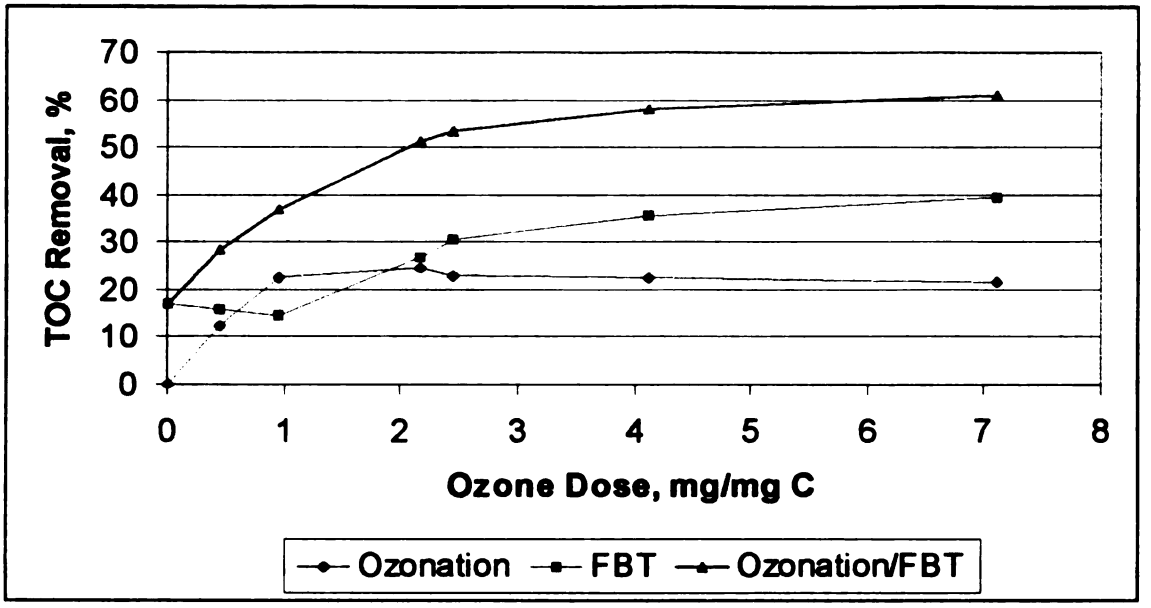


Figure 3.6. Effect of ozonation and FBT on TOC removal in unfractionated samples.

It can be seen in Figure 3.6 that the TOC removal by FBT with an ozone dosage of zero was approximately 16%. This TOC removal by FBT alone was not improved with the addition of ozone at doses 0.5 and 1.0 mg/mg C. These results show that at low ozone dosages, ozonation removed biodegradable organic compounds that could otherwise be removed by biological treatment. Therefore, the FBT efficiency was decreased at low ozone dosages as ozone removed some of the substrate that could have been utilized by the microorganisms in the FBR. The results from the apparent molecular weight distribution supported these results for ozone doses 0.5 and 1.0 mg/mg C. The TOC concentration of high molecular weight compounds was significantly reduced, however, there was no simultaneous increase in the TOC concentration of low molecular

weight compounds after ozonation (Figures 3.2 and 3.3). Therefore, this result indicated that the ozone was oxidizing the high and low molecular weight compounds simultaneously. At ozone dosages 0.5 and 1.0 mg/mg C, the ozonated samples (Figures 3.2 and 3.3) did not show any increase in TOC removal by FBT as compared to the TOC removal in the untreated water (Figure 3.1).

At ozone dosages greater than 1.0 mg/mg C, the TOC removal by FBT increased and the TOC removal by ozonation appeared to level off (Figure 3.6). Therefore, at ozone doses higher than 1.0 mg/mg C, ozone is no longer being used to oxidize organic carbon, but rather to produce biodegradable organic carbon that can be degraded in the FBR. This result suggests that the ozone was used more efficiently for the oxidation of higher molecular weight compounds into the lower molecular weight compounds at ozone doses greater than 1.0 mg/mg C. These TOC results correspond well with the apparent molecular weight distribution results at an ozone dose of 2.0 mg/mg C. The apparent molecular weight distribution results show an increase in lower molecular weight compounds (<1000 daltons) after ozonation at a dose of 2.0 and 7 mg/mg C, which consequently increased the biodegradability of the sample (Figure 3.4 and 3.5).

Higher TOC removal efficiencies by ozonation were expected at higher ozone dosages. Results show that the TOC removal by ozonation/FBT consistently increased with increased ozone dose (Figure 3.6). Similar studies support these results in that TOC removal has been shown to increase with increased ozone doses [14, 19]. The apparent molecular weight distribution results also suggested that the TOC removal in all molecular weight fractions after ozonation/FBT increased as the ozone dose increased.

3.2.7 Effect of FBT/ozonation at Ozone Doses 0.5 and 1.0 mg/mg C. The FBT/ozonation system was operated at ozone dosages of 0.5 and 1.0 mg/mg C without recycle. It was expected that ozone would be used more efficiently in the FBT/ozonation system than in the ozonation/FBT system. This hypothesis was based on the idea that the FBR would remove the lower molecular weight compounds that would otherwise be removed by ozone. Those compounds not removed by biological treatment were expected to be oxidized into biodegradable organic compounds by ozone.

The apparent molecular weight distribution results for the FBT/ozonation system operating at ozone dosages 0.5 and 1.0 mg/mg C are shown in Figure 3.7.

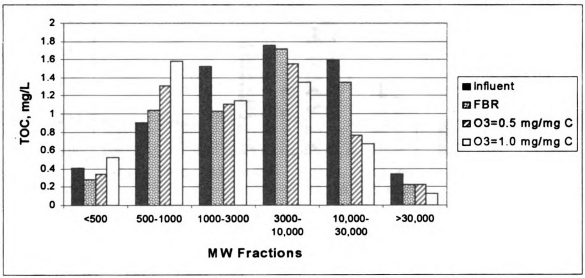


Figure 3.7. Effect of FBT/ozonation system at ozone doses 0.5 and 1.0 mg/mg C.

The results in Figure 3.7 are consistent with the hypothesis in that the TOC removal by FBT/ozonation is efficient at both ozone doses of 0.5 and 1.0 mg/mg C. The ozone oxidized the higher molecular weight compounds into lower molecular weight compounds, thereby decreasing the concentrations of compounds with apparent

molecular weight greater than 3000 daltons and increasing the concentrations of compounds with apparent molecular weight less than 3000 daltons. However, a more significant transformation of NOM by FBT/ozonation can be seen at the ozone dose of 1.0 mg/mg C compared to the ozone dose of 0.5 mg/mg C. Based on these results and results from other surrogate parameters, it was decided to use an ozone dose of 1.0 mg/mg C for the FBT/ozonation system.

The transformation of NOM during the FBT/ozonation system at an ozone dose of 1.0 mg/mg C can be seen in Figure 3.8.

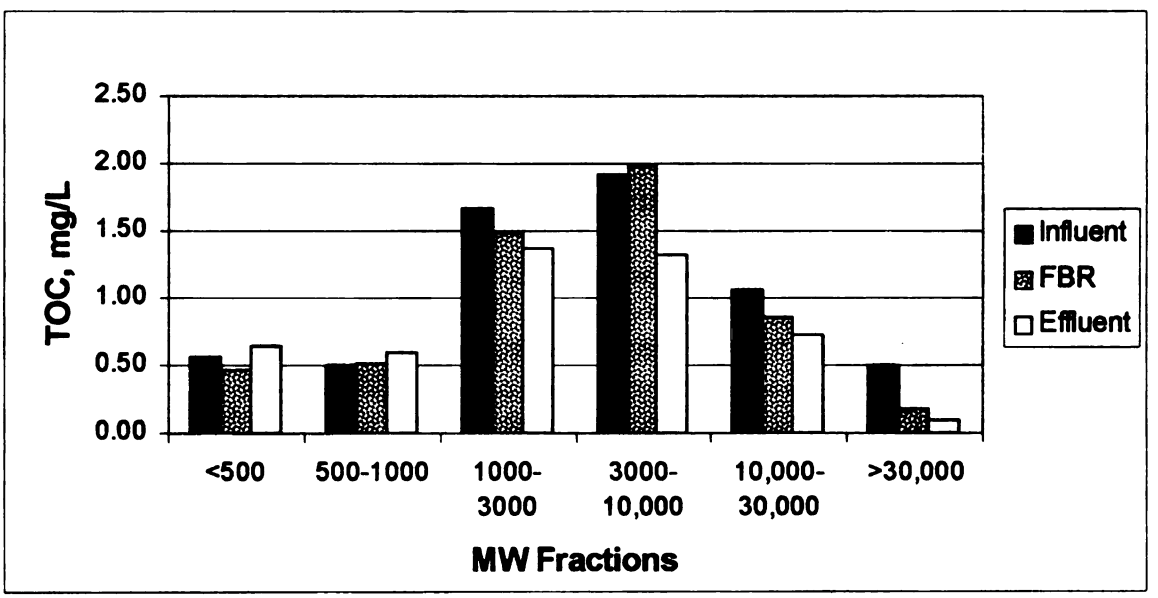


Figure 3.8. Effect of FBT/ozonation system at an ozone dose of 1.0 mg/mg C.

The results of the FBT/ozonation system at an ozone dose of 1.0 mg/mg C (Figure 3.8) are comparable to the results of the ozonation/FBT system at an ozone dose of 2.0 mg/mg C (Figure 3.4). The FBT system removed both high and low molecular weight compounds, and the ozone oxidized the high molecular weight compounds into low molecular weight compounds. There are slight differences in the middle molecular weight fractions (1000-3000 daltons and 3000-10,000 daltons) in Figures 3.7 and 3.8.

However, the differences are not significant and the same pattern can be seen between the low and high molecular weight fractions after each treatment process. Therefore, an ozone dose of 1.0 mg/mg C in the FBT/ozonation system increased the biodegradability of the water samples.

3.3 Conclusions

The TOC results obtained from the apparent molecular weight distribution study and the TOC removals in unfractionated samples were used to analyze the process performance of the ozonation/FBT and the FBT/ozonation systems. It was apparent from the results that ozone was not effectively used in the ozonation/FBT system. It is inefficient and not cost effective to use ozone for the removal of compounds that can be biologically degraded. Therefore, recycling the FBT effluent back to the ozone contactor would increase the efficiency of the ozonation/FBT system. Modifying the ozonation/FBT system to an FBT/ozonation system showed an even greater increase in the treatment efficiency. The FBT/ozonation system achieved similar results at an ozone dose of 1.0 mg/mg C as compared to the ozonation/FBT system at an ozone dose of 2.0 mg/mg C, thereby consuming ozone and reducing costs.

CHAPTER 4

PHASE III – RELATIONSHIP BETWEEN LOW MOLECULAR WEIGHT COMPOUNDS AND BIODEGRADABILITY

4.1 Objective

Based on the apparent molecular weight distribution studies on the FBT/ozonation system (See Figure 3.7), ozonation increased the fraction of lower molecular weight compounds, which consequently increased the removal efficiency by the FBT. This provided evidence that there was a correlation between the concentration of lower molecular weight compounds and the biodegradability of the sample. It was expected that low molecular weight compounds would be more easily biodegraded than high molecular weight compounds, and that as the concentration of low molecular weight compounds increased, the biodegradability of the sample would also increase. Therefore, further experiments were conducted to establish the relationship between the low molecular weight compounds and dissolved biodegradable organic carbon (BDOC) in the water samples.

4.2 Analytical Methods

4.2.1 Biodegradability Studies. Batch biodegradability experiments were conducted in which untreated water and FBT/ozonation effluent samples were recirculated through the biodegradability system for seven days (for description, see Chapter 2) to determine the BDOC concentration. Although the biocolumn in the biodegradability system removed all of the BDOC within five to six days, the samples were processed for seven days to ensure complete biodegradation of organic carbon. The

BDOC was determined by subtracting the TOC concentration of the biocolumn effluent from the TOC concentration of the biocolumn influent.

4.2.2 Ultrafiltration. The same untreated water and FBT/ozonation effluent samples that were recirculated through the biodegradability system were also processed by ultrafiltration. Several factors, including operating mode (batch vs continuous), membrane, and sample volume, were taken into consideration to develop a new ultrafiltration protocol to determine the concentration of low molecular weight compounds. Due to the large number of samples that needed to be processed in one day, it was necessary to operate the ultrafiltration system in batch mode rather than the continuous mode. Batch mode ultrafiltration allowed five different samples to be processed in one run, whereas continuous mode would only allow one sample at a time.

Also, the ultrafiltration membrane was chosen to represent the concentration of low molecular weight compounds. It was suspected that the compounds having an apparent molecular weight less than 500 daltons (MW500) were the most biodegradable fraction of NOM in the samples [14]. Therefore, it was decided, for several reasons, that the YC05 membrane, with an apparent molecular weight cutoff of 500 daltons, could be used to characterize the concentration of low molecular weight compounds.

The first reason was based on previous results presented in Chapter 2, which indicated that the TOC concentrations in the YC05 samples did not significantly vary from batch mode to continuous mode. On the contrary, the TOC concentrations for the other membranes did vary considerably based upon the processing method (Table 2.3). Therefore, operating the ultrafiltration system in batch mode with the YC05 membrane, the concentration of the NOM would not be affected to any significant extent. Also, the

TOC concentrations of samples processed through the YC05 membranes in batch mode were less affected by the increase in volume than those processed through the other membranes. Figures 2.9 – 2.13 and 2.14 – 2.18 showed that the slopes were smaller for the YC05 membrane than for any other membrane, which indicates that the increase in TOC due to increased volume was less significant for the YC05 membrane than the membranes with higher molecular weight cutoffs. Therefore, it was suspected that the concentration polarization and membrane rejection had the least affect on the samples processed through the YC05 membrane. Related research conducted by Logan and Jiang, 1990 [22], also proposed that the effect of membrane rejection on the YC05 membrane was not as consequential as the membranes with higher molecular weight cutoffs.

Additional experiments were conducted to determine the effect of volume on the TOC concentration when samples were processed in batch ultrafiltration mode through the YC05 membrane. The following procedures were used to process FBT/ozonation samples through the ultrafiltration membranes:

- Collect 0-40 mL, 40-80 mL, 80-120 mL samples.
- Discard 20 mL and then collect 100 mL composite sample.
- Discard 20 mL and then collect 80 mL composite sample.
- Discard 20 mL and then collect 0-50 mL, 50-100 mL samples.

The TOC concentrations determined for each procedure are illustrated in Figure 4.1.

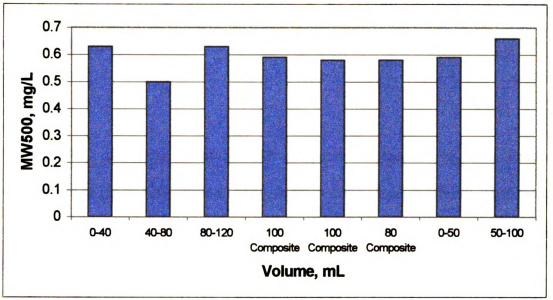


Figure 4.1. TOC concentrations of the low molecular weight fraction (<500 daltons) at different sample volumes.

Figure 4.1 shows that there is no significant difference in the TOC concentrations of the MW500 compounds in an 80 mL composite sample and a 100 mL composite sample. These results also indicate that the increase in volume did not significantly change the TOC concentration of the MW500 fraction. Therefore, it was determined that the first 20 mL of YC05 permeate would be discarded, and then a 100 mL composite sample would be collected for TOC analysis. All subsequent samples were processed by this same procedure through the YC05 membrane in batch mode and then analyzed for TOC.

Additional experiments were conducted with the established protocol (described above) to determine the analytical error. The same procedure was repeated several times using the same sample to determine the standard deviation. Samples from the FBT/ozonation system were simultaneously processed through the batch mode ultrafiltration system and statistical analysis was conducted on the TOC measurements. The average standard deviation for ten replicates of FBT/ozonation effluent was

0.03 mg/L. Processing replicate samples through the ultrafiltration cells ensured the reliability of the measurements.

4.3 Results

The TOC concentrations of MW500 compounds obtained using ultrafiltration were compared to the BDOC concentrations obtained using biodegradability experiments for the same samples. The goal was to establish a relationship between low molecular weight compounds and biodegradability.

Figure 4.2 shows a graph of the TOC concentration of MW500 compounds versus the BDOC concentrations in the samples.

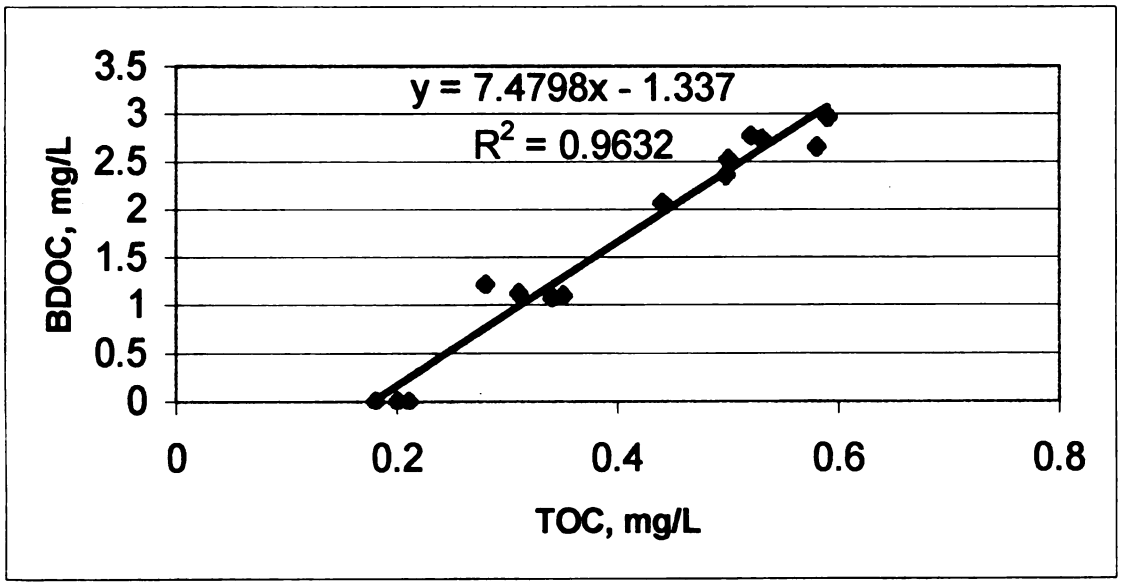


Figure 4.2. Relationship between the TOC concentration of MW500 compounds and biodegradability.

A linear relationship can be seen in Figure 4.2 between the low molecular weight compounds and the biodegradable organic compounds. These results indicate that there is a good correlation between the biodegradation potential and apparent molecular weight

compounds less than 500 daltons. The results show an increase in biodegradability with increasing TOC concentration of the MW500 fraction, providing further evidence that an increase in the concentration of smaller molecular weight compounds increases biodegradability.

4.4 Conclusions

The relationship between MW500 compounds and BDOC is useful for the evaluation of biodegradation potential of NOM in the water samples. Therefore, water utilities can use ultrafiltration as a cost effective and time saving method over batch biodegradability experiments for determining biodegradation potential.

CHAPTER 5

THESIS SUMMARY AND RECOMMENDATIONS

5.1 Thesis Summary

The overall objective of this study was to use apparent molecular weight distribution as a surrogate parameter to evaluate a combined ozonation and FBT system for the removal of NOM. A review of NOM and the significance it has in drinking water treatment was presented in Chapter 1. Also a review of the literature related to the applicable treatment processes and the use of apparent molecular weight distribution was also presented in Chapter 1. Three experimental systems, described in Chapter 2, were utilized to investigate the effect that ozonation, FBT, and combined treatment had on the transformation of NOM in Huron River water.

This study was broken down into three main sections, Phases I, II, and III, which are described in Chapters 2, 3, and 4, respectively. The primary goal of Phases I and II was to develop an apparent molecular weight distribution protocol that could be used to evaluate the transformation of NOM in water at different stages in the combined ozonation and biological treatment processes. Several studies were conducted in the first phase of this study to examine the effect of changing experimental conditions on the TOC concentrations in each molecular weight fraction. Results showed that although a change in sample volume caused a change in individual TOC concentrations, there was no significant effect on the trends in the TOC concentrations throughout the treatment stages. Therefore, as long as consistent experimental conditions are maintained,

ultrafiltration results are useful for comparative purposes. Several experiments were also conducted to evaluate the error associated with each of the molecular weight fractions.

In Phase II of this study, the apparent molecular weight distribution protocol developed in Phase I was used to evaluate FBT and combined ozonation/FBT. Results showed that FBT removed both high and low molecular weight compounds even in the absence of ozone. The results also showed that when ozonation was utilized, ozone oxidized both high and low apparent molecular weight compounds at ozone doses lower than 1.0 mg/mg C. Therefore, the ozone was used inefficiently at low dosages for the removal of compounds that could otherwise be biologically degraded. However, at ozone doses greater than 1.0 mg/mg C, the high molecular weight compounds were partially oxidized by ozonation into lower molecular weight compounds. Therefore, ozonation only increased the biodegradability of the NOM when the ozone dose was greater than 1.0 mg/mg C. These results were verified by the TOC removal results (Figure 3.6) which showed that the TOC removal by FBT decreased at ozone doses 0.5 and 1.0 mg/mg C. Therefore, TOC results also indicated that ozone was used more efficiently to produce BDOC at ozone doses greater than 1.0 mg/mg C.

Apparent molecular weight distribution was also used in Phase II to evaluate the treatment process after modifications were made to the experimental system. The ozonation/FBT system was rearranged as FBT/ozonation in order to attempt to improve the treatment efficiency. Biological treatment was used to remove biodegradable organic compounds that would otherwise be removed in the ozonation stage. The evaluation of the FBT/ozonation system by apparent molecular weight distribution showed that the ozone was used much more efficiently when ozonation followed FBT. The

FBT/ozonation treatment effectiveness at an ozone dose of 1.0 mg/mg C was comparable to the original ozonation/FBT results achieved at an ozone dose of 2.0 mg/mg C. Therefore, it was determined that ozone was used much more efficiently in the FBT/ozonation system as compared to the ozonation/FBT system. Based on the results of this study, apparent molecular weight distribution was shown to be a useful tool to monitor the treatment process performance and develop optimization strategies. Apparent molecular weight distribution is also a useful tool to determine the appropriate treatment technique for specified source waters.

The last phase of this study, described in Chapter 4, focused on the development of a model to relate low molecular weight compounds to biodegradability. Several batch biodegradability studies were conducted to determine the BDOC concentration in untreated and FBT/ozonation samples. The BDOC results were used for comparison with the TOC results of the fractions containing compounds with an apparent molecular weight less than 500 daltons. A good correlation was established between the apparent molecular weight compounds less than 500 daltons and BDOC. Therefore, the use of ultrafiltration to determine the concentration of the compounds having an apparent molecular weight less than 500 daltons was shown to be a practical method of evaluating the biodegradation potential in a water sample. It would be cost effective and time saving for water treatment utilities to use ultrafiltration rather than batch biodegradability experiments for the determination of biodegradation potential.

5.2 Recommendations for Future Research Efforts

Future experiments would further support the results obtained in this apparent molecular weight distribution study. The individual molecular weight fractions were primarily characterized by TOC for this project, but these results could be further supported by measurements of UV absorbance and THMFP for the same samples. The ratio of UV absorbance to TOC would be another parameter for evaluating ozonation. A decrease in this ratio would indicate that the ozone was oxidizing UV absorbing functional groups rather than completely oxidizing organic carbon to carbon dioxide and water [15]. Also, the correlation between THM yield, which is the ratio of THMFP to TOC, and the apparent molecular weight would indicate the removal of DBP precursors by the treatment process. Past studies have shown a positive correlation in which THM yield increases with apparent molecular weight [4], although in some cases, lower molecular weight compounds are more reactive and produce higher THM yield [23].

In future studies, additional analytical methods should be investigated for comparative purposes. The comparison of ultrafiltration with GPC would ensure that the trends in NOM throughout the treatment processes are independent of the specified analytical technique. Although past research has shown that GPC produces higher apparent molecular weight values than ultrafiltration, both methods should display the same relationship between the organic matter in the samples and the transformation as it passes through the treatment stages [4].

Also, it is recommended that membrane rejection be taken into account by the Logan and Jiang method [22], when batch ultrafiltration is used for apparent molecular weight distribution. This would ensure that membrane rejection does not cause an

underestimation of low molecular weight compounds in the apparent molecular weight distribution. Rejection coefficients need to be determined for each membrane and sample processed in batch mode ultrafiltration by monitoring the instantaneous changes in the permeate concentrations. The rejection coefficient can then be used to account for the rejected molecular weight fractions below the membrane cutoff.

Phase III of this study established a relationship between biodegradability and the low molecular weight compounds based on the apparent molecular weight fraction less than 500 daltons. However, to support these results, additional experiments should be conducted to determine the relationship between biodegradability and higher molecular weight compounds. This can be done by using the Phase III protocol, but use the YM1, YM3, YM10, and YM30 membranes rather than the YC05 membrane. If a relationship exists, the slopes will allow a comparison between biodegradability and various apparent molecular weight compounds. The TOC concentrations of the MW500 compounds were extremely low, which caused the instrumental error to be more significant than in the higher molecular weight fractions which contained higher TOC concentrations. Also, operating the ultrafiltration system in series rather than in parallel would reduce some of the analytical error caused by membrane rejection.

Lastly, preliminary experiments were conducted using the bench-scale ozonation system to investigate the effects of ozone dose, retention time, and temperature on the ozonation of low molecular weight compounds (<500 daltons) in raw and biodegraded water samples (Appendix A). However, not enough data was collected to establish any conclusions, and therefore, it is recommended that further experiments be conducted to support the preliminary results obtained.

APPENDIX A

APPENDIX A

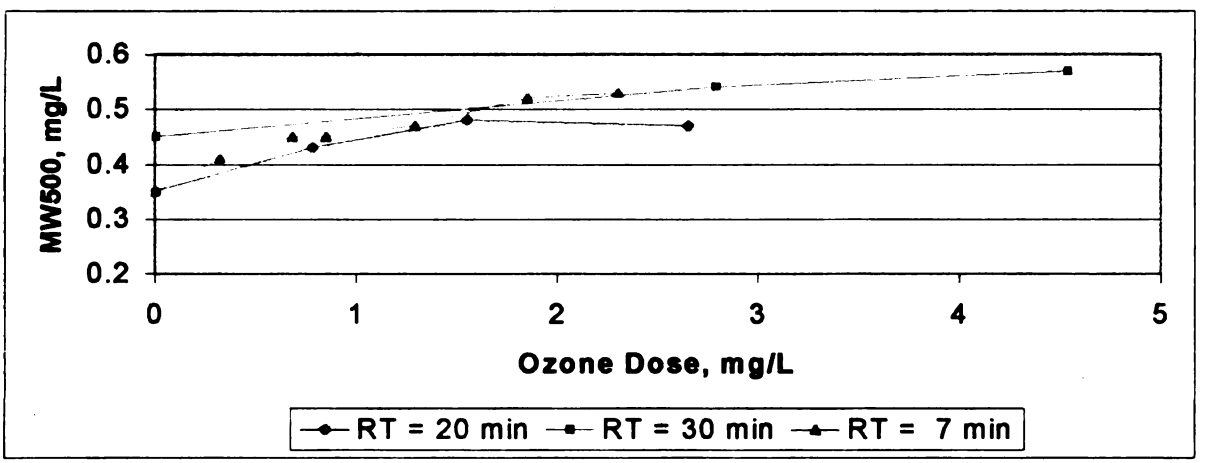
A.1 Objective

Preliminary experiments were conducted using the bench-scale ozonation system to determine the effect of retention time, temperature, and ozone dose on the TOC concentration of compounds with the apparent molecular weight less than 500 daltons.

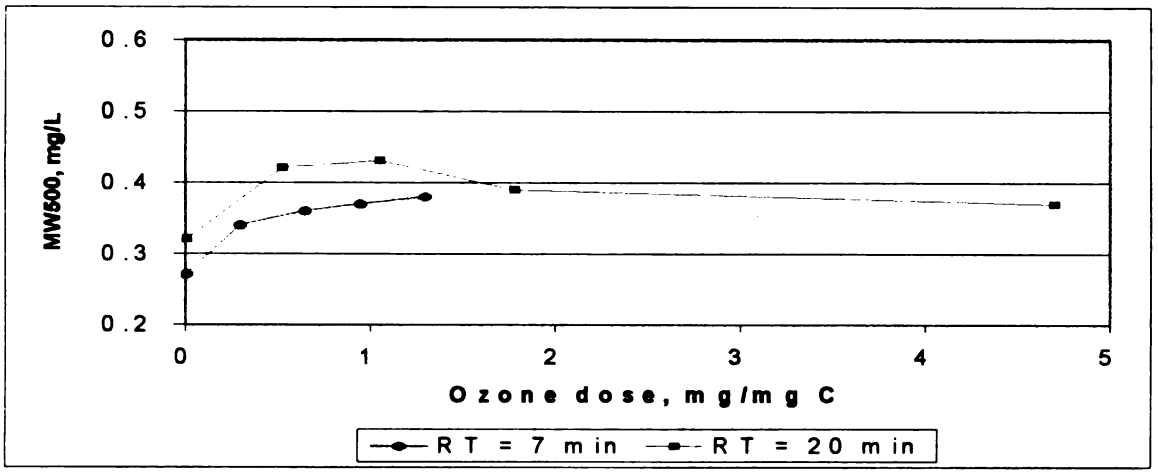
A.2 Analytical Methods

Several preliminary experiments were conducted using the ultrafiltration procedure described in Phase III (See Chapter 4). Untreated Huron River water and biologically treated Huron River water was processed through the bench-scale system at seven and twenty minute retention times to determine the effect of retention time on the TOC concentration in the apparent molecular weight compounds less than 500 daltons. Experiments were conducted at various ozone doses and temperatures.

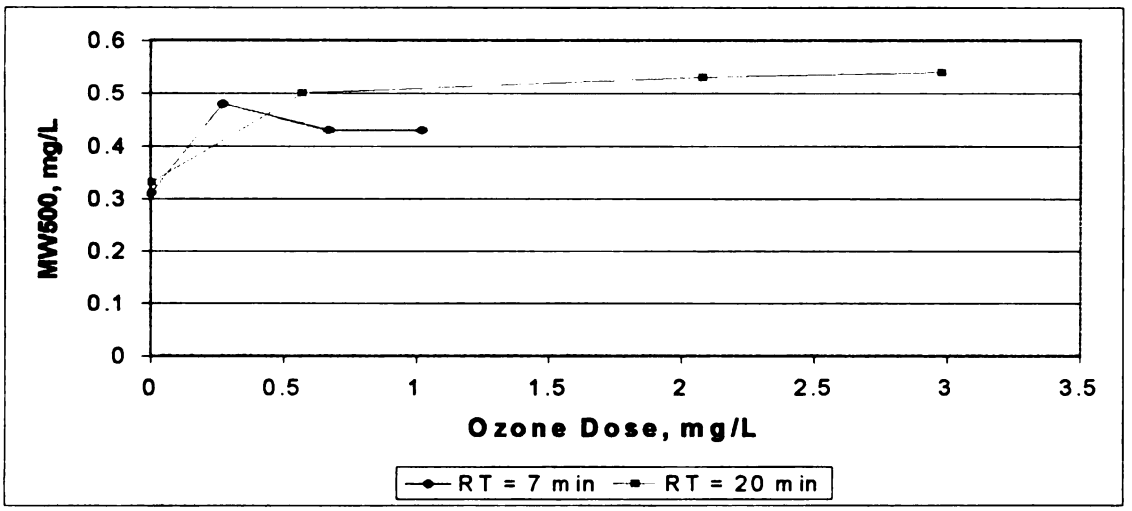
A.3 Results



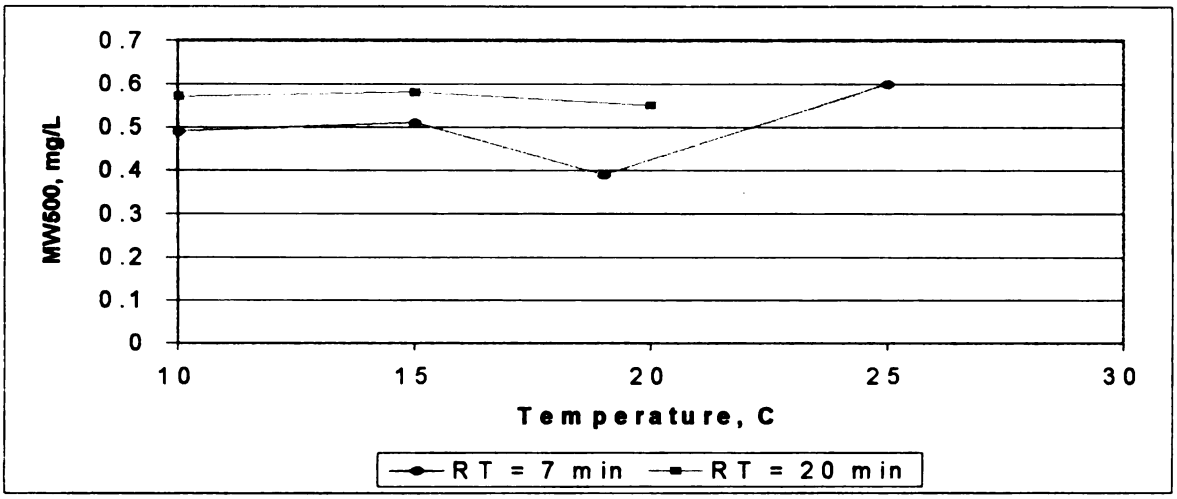
A.1 Effect of retention time on low molecular weight compounds (<500 daltons) during ozonation of untreated Huron River water. (11/25, 12/2, and 1/6)



A.2 Effect of retention time on low molecular weight compounds (<500 daltons) during ozonation of biologically treated water (1/13, 12/16).



A.3 Effect of retention time on low molecular weight compounds (<500 daltons) during ozonation of untreated Huron River water. (1/12, 2/3)



A.4 Effect of retention time during ozonation of untreated Huron River water at various temperatures. (1/6, 1/20)

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